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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

[illegible]

Winter 1964-1965

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TECHNICAL PROGRESS REVIEWS

To meet the needs of industry for concise summaries of current atomic developments, the Atomic Energy Commission is publishing this series, Technical Progress Reviews. Issued quarterly, each of the reviews digests and evaluates the latest findings in a specific area of nuclear technology and science.

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Nuclear Safety, Wm. B. Cottrell, W. H. Jordan, and associates, Oak Ridge National Laboratory

Power Reactor Technology, W. H. Zinn and J. R. Dietrich, Combustion Engineering, Inc., Nuclear Division

Reactor Fuel Processing, Stephen Lawroski and associates, Chemical Engineering Division, Argonne National Laboratory

Reactor Materials, R. W. Dayton, E. M. Simons, and associates, Battelle Memorial Institute

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A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are M. Ader, J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

New Domestic and Foreign Plans

The General Electric Company (GE) announced that it expects to begin construction of a chemical processing plant at an unspecified site in the western United States in 1967. The total cost of the project, including design, construction, and preoperation and testing, is estimated to exceed $15 million, and operation is to begin by 1971. The plant will use the fluoride-volatility process which GE has been studying jointly with the Allied Chemical Company. This study agreement ended in April 1964, and Allied will have no role in the present GE project. It is reported, however, that Allied has secured rights to GE patents, now pending, which claim the solution of a major problem that has delayed the commercial application of the fluoride-volatility process. Allied is said to be looking forward to launching a program of its own when "the time is ripe."[1]

General Electric is considering the distribution of nuclear power plants in California and the possibility of a site at Hanford, where the U. S. Atomic Energy Commission (AEC) is promoting a variety of nuclear-industrial operations. Although California utilities themselves have ambitious long-range plans for nuclear power, the present power-supply situation, and hence the timing of new projects, is not clear. The design capacity of the proposed new GE plant was not announced; proponents of the fluoride-volatility process have maintained that it opens up the possibility of building relatively small, flexible plants that can operate at least as economically as larger plants using conventional processing technology.[1]

Westinghouse and Dow Chemical Company have organized a joint venture to develop new methods of processing spent fuel and fabricating plutonium. They plan to build a $1.7 million recycle fuel laboratory and pilot-plant facility for operation by the end of 1965. The two companies will share these costs equally and will each contribute $500,000 for an operating budget. Hanford is one of several sites being considered.[1,2]

The Atomic Energy Commission of Japan has proposed to the Japanese government that a fuel-processing plant be built and operated by the Japan Atomic Fuel Corporation. (An earlier announcement was cited in the Fall 1963 issue of *Reactor Fuel Processing*.) The plant would be financed entirely by the government, would have a capacity of 0.7 ton per day, and would be capable of handling fuels of all enrichments. One reason for the plan was said to be the high cost of overseas shipping of spent fuel. A preliminary design of the plant is under way.[3]

Commercial Development of Processing at Hanford

The AEC announced that the research laboratory facility formerly called Hanford Laboratories has been renamed the Pacific Northwest Laboratory. The new name applies now that the Battelle Memorial Institute of Columbus, Ohio, is the Commission's operating contractor of the laboratory.[4]

An invitation has been extended by AEC to private industry to submit proposals for participation on a purely commercial basis in a large-scale fission-product recovery program at the Hanford plant. In its broader aspect the invitation also extends to proposals for the operation of facilities in the chemical separations area, which includes separation of plutonium and uranium from irradiated reactor fuel and waste-management facilities.[5]

Proposals for the management and operation of the AEC plutonium-production reactors and

the fuel-fabrication area of the Hanford plant have also been invited by the AEC as part of the Hanford segmentation program. This program results from a mutual agreement in January 1964 between AEC and GE, which has been the sole operator of the plant[6] since 1946.

Transportation of Irradiated Fuel

The problem of safe and economical transportation of radioactive materials, such as spent fuel elements, is complex and difficult. A review of design tests and economic analyses has been given in the Winter 1963–1964 issue of *Reactor Fuel Processing* and in a recent paper by Thompson.[7] A recent review of the safety aspects of spent-fuel transport is provided by a U. S. paper presented at the 1964 Geneva Conference.[8] In this paper the chief design problems are identified as shielding, heat removal, criticality prevention, and cask integrity under accident conditions.

Although a great deal of clarification of this problem has taken place through progress made in methods of assessing the safety of cask design, much remains to be done in analyzing accidents and in establishing shipping and design criteria in such a manner that the overall costs and economic risks can be evaluated.[8]

Cost studies of shipping irradiated fuel elements from a reactor to a processing plant are under way at Oak Ridge National Laboratory.[9] In these studies casks with adequate shielding and cooling are designed, and fuel-cycle optimizations are made, for a variety of reactor- and fuel-management conditions. The existence of optimal conditions may arise in several ways. A longer cooling time reduces the shielding requirement and heat loads; however, this reduction may be offset by increased fuel-inventory charges for the cooling period. An increase in the number of elements per cask tends to lower the cask weight (and cost) per fuel element, but the increasing difficulty of heat removal of a larger number of elements finally has an overriding effect in the opposite direction. Also, fuel management at a central processing facility must consider batch size and turnaround time. If the optimization considers processing costs in addition to shipping and inventory charges, a number of casks larger than the minimum number to keep up with reactor discharge may be required. In this case the shipping cost is larger than if it were calculated to minimize the total of shipping and cooling costs only.

Fuel shipping costs calculated for typical reactors by the computer cost codes of this study are shown in Tables I-1 and I-2. Economic ground rules for these tables are as follows: a freight rate of $1.93 per 100 lb (full) and $1.81 per 100 lb (empty), a shipping distance of 1000 miles each way, a handling cost of $500 per round trip, an insurance rate of 0.2% of the fuel value, a fixed-charge rate on casks of 15% per year, a cask cost of $1.00 per pound, and a maximum shipping weight of 140,000 lb.

In Table I-1 the fuel management did not consider the processing plant, and the number of casks was the minimum number required to

Table I-1 TYPICAL CALCULATED FUEL SHIPPING COSTS* ACCORDING TO THE MYRA CODE*

	Commonwealth Edison, Dresden	Yankee	CPPD, Hallam	Consolidated Edison, Indian Point	Westinghouse 1000-Mw(e) PWR study	Desalinization reactor, 25,000-Mw(t) study
Costs, dollars/kg of reference material						
Freight	1.20	1.75	1.13	2.02	1.66	0.86
Handling	0.10	0.20	0.12	0.22	0.18	0.10
Fixed charges on casks	0.71	1.12	2.08	1.71	0.43	0.15
Insurance	0.16	0.43	0.45	1.25	0.26	0.05
Total shipping cost	2.17	3.50	3.78	5.20	2.53	1.16
Reference material	Total U	Total U	Total U	Total U + Th	Total U	Total U
Cooling time, days	90	90	90	90	90	120
Burnup, Mwd/metric ton of reference material	10,000	8200	8800	21,000	24,000	8000
Specific power, Mw/metric ton of reference material	11.9	18.3	8.8	35	25.8	11.7

*Computer code for shipping-cost calculations.

Table I-2 PRELIMINARY RESULTS OF SHIPPING-COST CALCULATIONS[9] (ADVANCED CONVERTER STUDY USING NORA CODE*)

Reactor	Average burnup, Mwd/metric ton of reference material	Cooling time, days	Shipping cost, dollars/kg of reference material	Reference material
PWR	20,000	150	3.94	Uranium
	25,000	180	4.08	
	30,000	180	3.71	
	35,000	180	4.02	
Seed-blanket	50,000	240	9.69	Thorium
	60,000	240	9.67	
	70,000	240	9.78	
	80,000	270	9.86	
	90,000	270	10.20	
SSCR	20,000	240	3.94	Thorium
	25,000	240	4.64	
	30,000	270	4.04	
	35,000	270	4.69	
	40,000	300	4.12	
D_2O-UO_2	14,000	360	2.02	Uranium
	15,400	360	2.09	
	17,000	360	2.37	
	20,000	360	2.85	
D_2O-ThO_2	15,000	270	3.35	Thorium
	22,000	300	3.98	
	30,000	330	4.44	
TARGET	40,000	120	33.04	Thorium
	51,400	150	32.67	
	60,000	150	32.70	
	70,000	150	32.92	
SGR	25,000	150	3.78	Uranium
	35,000	90	5.01	
	45,000	60	5.51	

*A computer code for shipping-cost calculations.

keep up with the rate of discharge from the reactor. In Table I-2 somewhat higher costs are due (in part) to a larger-than-minimum number of casks based on processing-plant considerations and on greater average fuel exposures in the reactor.[9]

Cost Studies for Processing of Converter-Reactor Fuel

As part of an overall comparative evaluation made at ORNL[9] of advanced converter reactors, especially thorium-fueled converters, costs were estimated for aqueous processing of irradiated fuel from the reactor types listed in Table I-2, for a range of burnup values around the reference figure shown. Capital and operating costs were estimated for each hypothetical processing plant. The rules specified a fixed-charge rate of 22.5%, with alternative values of 15 and 30%, to be applied to capital investment to cover the annual cost of depreciation, interest on debt capital, return on equity capital, federal income taxes for corporations, other taxes, and property and liability insurance for privately owned plants.

The calculated costs were based on the estimates of Farrow,[10] with modifications of the basic Purex process as deemed appropriate for each fuel type to allow for differences in head-end treatment and fertile and fissile throughput rates, plus added costs for krypton removal from off-gases, ultimate waste disposal, and escalation to 1964 price levels. The relative insensitivity of total fuel-processing capital and operating costs to production rate gives rapidly decreasing unit-production costs with increasing plant size. However, fixing the size of a nuclear power industry served by one single-purpose processing plant at a constant 15,000 Mw(e) tended in the present study to minimize the difference between reactor types as far as processing-cost contribution to unit electricity costs (mills per electrical kilowatt-hour) is concerned, since wide differences in

the amount of fuel to be processed per year are associated with smaller differences in the total annual processing costs.

In the typical cases of this study presented in Table I-3, the higher burnup fuels tend to have higher processing costs in dollars per metric ton but lower costs in mills per kilowatt-hour. It should be emphasized, however, that the processing cost is not necessarily the controlling factor in overall cost evaluation. For the reactors in this study, for example, fabrication costs generally were higher than processing costs and varied more between reactors. The overall fuel-cycle evaluation, including fabrication and reactor costs, is in preparation.[9] It is understood, from sources within the AEC, that this evaluation will omit any reference to the seed-blanket reactor. The information reported above is preliminary and was not taken from the primary source which has not been released.

Radiochemical Plant Safety

Liability of Maximum Accidents

Because of the large quantities of radioactive material that would be handled in large radiochemical plants for fuel processing or radioisotope source production, the public hazards of such plants may exceed those of nuclear reactor operation. The normal design of radiochemical plants is such as to prevent the re-

Table I-3 TYPICAL SPENT-FUEL PROCESSING COSTS FOR ADVANCED CONVERTER STUDY:[9] SINGLE-PURPOSE PLANTS

[Basis: 15,000-Mw(e) Total Capacity, 80% load Factor;
1000 Mw(e) per Reactor Except 500 Mw(e) for Seed-Blanket Reactor;
150 Days Minimum Cooling Time Before Processing; and
310 Operating Days per Year (Processing Plus Turnaround)]

	Type of Reactor						
	PWR	SBR	SSCR	D_2O-U	D_2O-Th*	TARGET	SGR
Mwd/metric ton, U or Th	25,000	70,000†	30,000†	15,400	22,000†	51,400†	35,000
Thermal efficiency, %	31.1	28.8	31.2	26.8	26.8	45.8	43.6
Metric tons/batch, U or Th	38.7	77.4†	66.3†	23.0	12.2†	12.9†	12.8
Kg/batch, Pu or U	380	3,230†	2,635†	92.0	215†	445†	88.0
Metric tons/year, U or Th	563	217†	468†	1,060	784†	186†	287
Kg/year, Pu or U	5,520	9,040†	18,600†	4,240	13,800†	6,410†	1,970
Kg/year, fission products	14,100	15,200	14,000	16,300	16,300	9,560	10,000
Batches/year	14.5	2.80	7.06	46.1	64.3	14.4	22.4
Processing days/year	194	288	254	155	155	195	155
Processing rates							
Metric tons/day, U or Th	2.90	0.753†	1.84†	6.85	5.06†	0.954†	1.85
Kg/day, Pu or U	28.5	31.4†	73.2†	27.4	89.0†	32.9†	12.7
Total capital investment,‡ millions of dollars	71.7	60.4	71.2	79.9	81.9	63.6	66.1
Annual operating cost, millions of dollars	6.7	5.1	6.5	7.6	7.9	5.5	5.8
Annual charge for ultimate disposal, millions of dollars	3.2	3.3	3.2	3.4	3.4	2.5	2.6
At 15% fixed-charge rate							
Millions of dollars/year	20.7	17.5	20.4	23.0	23.6	17.5	18.3
Dollars/metric ton	36,800	80,600	43,600	21,700	30,100	94,100	63,800
Mills/kw(e)-hr	0.197	0.166	0.194	0.219	0.224	0.166	0.174
At 22.5% fixed-charge rate							
Millions of dollars/year	26.0	22.0	25.7	29.0	29.7	22.3	23.3
Dollars/metric ton	46,200	101,000	54,900	27,300	37,900	120,000	81,200
Mills/kw(e)-hr	0.247	0.209	0.244	0.276	0.283	0.212	0.222
At 30% fixed-charge rate							
Millions of dollars/year	31.4	26.5	31.1	35.0	35.9	27.1	28.2
Dollars/metric ton	55,800	122,000	66,500	33,000	45,800	146,000	98,300
Mills/kw(e)-hr	0.299	0.252	0.296	0.333	0.341	0.258	0.268

*The burnup for the D_2O-Th case is for the core only, but the number of metric tons per batch and the number of metric tons per year include the blanket also. For all the other reactors, the numbers represent averages over one reactor-discharge batch.

†The dagger indicates that the fertile material is thorium and that the fissionable material is uranium.

‡Of the total investment, 6.2 to 7.0% is in land, startup, and working capital; the balance is the cost of the processing plant in each case.

lease of radioactive material outside the plant. The unique accident, criticality, is in itself minor with regard to off-site consequences. However, in the improbable but conceivable occurrence of simultaneous failure of containment, occurrence of fire or explosions that may disperse radioactive material, and meteorological conditions favoring local "fallout," the consequences of such serious accidents have been predicted in order to form a basis for estimating the upper limit of liability. In a recent report such potential economic losses were calculated for 17 isotopes.[11] (An earlier report of similar calculations was given in the Winter 1963–1964 issue of *Reactor Fuel Processing*.)

The present report of Guthrie and Nichols estimates that accidents having any likelihood of occurring in radiochemical plants with containment and engineered safeguards would not result in a monetary loss due to damage to the surroundings in excess of the limits of private insurance currently said to be available ($60 million). The more hazardous isotopes (e.g., ^{90}Sr, ^{238}Pu, ^{239}Pu, and ^{244}Cm) could well be handled in quantities that could (theoretically) result in off-site damage in excess of $60 million; such accidents, however, are considered to have an extremely low probability of occurrence.[11]

The proposal of the AEC with respect to private liability and government indemnification of the Nuclear Fuel Services, Inc. (NFS), processing plant (previously cited in the Summer 1964 issue of *Reactor Fuel Processing*) established, on an interim basis, $20 million as the amount for private liability and $500 million for government indemnification.

Safety and Siting Considerations in the Design of the NFS Fuel-Processing Plant

The fuel-processing plant now being constructed in western New York State by NFS is the first privately owned production facility of this type. The NFS plant was previously reviewed in *Reactor Fuel Processing*, 6(4): 1 (1963). In September 1964 the construction was about 50% completed. The target date[12] for completion is April 1965. A detailed safety analysis of the NFS plant was made in conjunction with the license application for the plant.[13] A review of the salient features of the safety and siting considerations was presented in a paper[14] given at the 1964 Geneva Conference.

The baseline process at NFS is a chop-leach head-end (nitric acid dissolution) and Purex solvent extraction for processing 1000 kg of low-enriched UO_2 per day clad in stainless-steel or zirconium alloy tubes. In addition, there is to be equipment for the dissolution of zirconium-uranium alloy fuels in a HNO_3-HF mixture and for nitric acid dissolution of uranium and aluminum-uranium or molybdenum-uranium alloy fuels. Fuels are cooled 150 days before processing.[14]

A number of factors were involved in site evaluation. Under existing U. S. law, radioactive waste storage must be done on land owned by either the federal or a state government. An economic advantage appeared to accrue in locating the processing plant on the waste-storage site owned by New York State under the jurisdiction of the New York State Atomic and Space Authority. This site is in a region of low population density and has features of meteorology and geology which have been considered to meet the safety and siting requirements for radiochemical plants. These requirements are, in general, more stringent than for waste storage. Important geological features are the surface deposits of granular glacial material, the underlying and almost completely impermeable silty till, and the substrata of sandy tills and shales. Each of these strata has significant ion-exchange properties.[14]

An important aspect of the plant safety analysis concerns the radioactivity discharged from the plant under both normal and abnormal conditions. The plant effluents are discharged to the following points: (1) to the atmosphere via the air exhaust stack, (2) to a local creek in the

Table I-4 LIMITING CASES FOR RADIOLOGICAL SAFETY IN NFS PLANT OPERATION[14]

Effluent	Isotope of limiting activity	Limiting mode of exposure
Normal Operation		
Stack gas discharge	^{85}Kr	Breathing and immersion
	^{131}I	Deposition in pasturage and uptake in milk
Liquid discharge	Tritium (^{3}H)	Allowable concentration for unrestricted use
Abnormal Operation		
Release in criticality incident	Iodine	Thyroid dose

case of the low-level liquid waste, (3) to the high-level liquid-waste storage tanks, and (4) to the solid burial ground. In normal operation there is no discharge from the high-level liquid-waste storage. The low-level liquid wastes are put through a general-purpose evaporator, and the condensate can be put through a cation-exchange contactor. The resulting liquid effluent (about 10,000 gal/day) is dispersed in the local creek system with a safety factor relative to permissible release levels. Fission-product tritium presents a special problem since there is no way to remove it from the aqueous waste streams once it is present as tritiated water. Special analytical techniques are required to discriminate between tritium and other activity, and there is a lower safety factor for tritium than for other isotopes with respect to the environmental release. (For a discussion of the tritium waste-disposal problem, see Sec. IV of this issue.)

Active solids are buried in silty till; safety with respect to retention of buried activity is favored by the circumstance that the mobile component of the solid activity is in very low concentration, whereas the high-level activity in the buried solids waste is immobile under existing conditions.[14]

Analyses of abnormal conditions (possible accidents) are discussed in the paper. Special consideration is given to the iodine hazard; iodine is normally removed from the gaseous effluent by silver reactors and other equipment. The most critical or limiting isotopes in the plant effluents have been identified.[14] These are given in Table I-4.

Table I-5 BRITISH PATENTS CONCERNING PREPARATION OR PROCESSING OF REACTOR FUELS

Title	Patent No.	Date
Fluidized Solids Process and Recovery of Uranium from Zirconium-Type Fuel Elements	925,178	Mar. 15, 1960
Vibration Compaction	925,186	Dec. 21, 1960
Nuclear Fuel Material	926,632	Dec. 23, 1959
Improved Stripping of Uranium from Organic Extractants	926,858	Mar. 24, 1961
Flame Denitration and Reduction of Uranium Nitrate to Uranium Dioxide	928,861	Feb. 7, 1961
Separation of Curium and Americium	930,966	June 15, 1961
Plutonium Recovery from Neutron-Bombarded Uranium Fuel	931,632	June 7, 1961
Uranium Extractant for Phosphoric Acid Liquors	932,675	Mar. 30, 1961
Protected Nuclear Fuel Element	933,091	Feb. 6, 1962
Method of Preparing a Fuel Element for a Nuclear Reactor	933,519	Jan. 15, 1962
Method of Making Fuel Bodies	933,552	Dec. 23, 1959
Recovery of Uranium from Zirconium-Uranium Nuclear Fuels	933,797	June 7, 1961
Aluminum Cladding Dissolution	933,807	Dec. 4, 1961
Separation of Uranium Metal from Oxides and Slag in the Reduction of Uranium Tetrafluoride	934,025	Mar. 28, 1962
Separation of Protactinium from Molten Salt Reactor Fuel Compositions	934,899	June 5, 1961
Preparation of UO_2 for Nuclear Reactor Fuel Pellets	937,330	June 29, 1961
Fused Reactor Fuels	938,117	May 18, 1960
Method for Obtaining Plutonium Metal and Alloys of Plutonium from Plutonium Trichloride	938,925	Feb. 3, 1961
Processing of Uranium-Metal-Containing Fuel Elements	939,384	Feb. 6, 1962
Preparation of Actinide-Aluminum Alloys	939,385	Feb. 6, 1962
Dimensionally Stable, Corrosion Resistant Nuclear Fuel	940,565	Feb. 6, 1962
Method of Making Fuel Bodies	941,824	Oct. 11, 1962
Controlled Nuclear Reactor Dispersions and Method of Making	941,825	Oct. 12, 1962
Method for Separating Transplutonium Elements from Rare Earth Fission Products	943,441	Aug. 28, 1961

Bibliographies and Patents on Fuel Processing

An annotated bibliography of literature in the field of processing of irradiated reactor fuels and breeding materials has been compiled by Jacobs.[15] This is a supplement that updates, through Jan. 15, 1964, a compilation (TID-3312) originally published in 1958. A total of 1035 additional references (and abstracts) are presented. References are grouped by process type under the major headings of Head-End Processing (Feed Preparation) and Fuel Material Separation and Decontamination. Sections are included on criticality, safety, commercial aspects, and economics. Author, corporate author, and report number–availability indexes are included.

An annotated bibliography of literature in the field of radioactive waste processing and disposal has been compiled by Davis and Voress.[16] This bibliography supplements previous publications TID-3311, TID-3555, and TID-3555 (Suppl. 1). A total of 989 references (and abstracts) from the period June 1962 to January 1964 are presented. The references have been arranged by subjects, including sections on commercial utilization and economics. Author, corporate author, and report number–availability indexes are included.

The AEC has announced the titles of 62 AEC-owned British patents on which it will grant licenses for royalties. Inquiries with respect to a license on any of these patents should be addressed to the office of Assistant General Counsel for Patents, Atomic Energy Commission, Washington, D. C. 20545. Of these patents, the titles directly concerning preparation or processing of reactor fuels are given in Table I-5; abstracts of all 62 patents are available from the AEC.[17]

(W. J. Mecham and A. A. Jonke)

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Miscellaneous studies have been continued on the modification and extension of aqueous processing methods to the newer types of reactor fuels that are used or proposed for use in power reactors. Improvements and broadened applications of solvent-extraction techniques are reviewed.

Preparation of Fuels for Recovery

Recent work on shearing of fuel tubes containing uranium dioxide, on dissolution of zirconia, zirconium alloys, sintered aluminum powder, and refractory oxides, and on treatment of graphite and carbide compositions is discussed.

Mechanical Processing Methods

Further work is reported from Oak Ridge National Laboratory (ORNL)[1,2] on cutting up second-generation power-reactor fuels using the 250-ton shear. Previous work was discussed in this publication.[3,4] Simulated fuel consisting of UO_2 pellets clad with 30-mil-wall 0.42-in.-OD Zircaloy-2 tubes (Consolidated Edison core B) was sheared in a bundle of 77 loose tubes. The comparative particle-size fractions obtained from this fuel as well as from a stainless-steel-clad UO_2 fuel are shown in Fig. II-1. The shearing force was 71 to 92 tons for zirconium-clad fuel bundles compared to 63 tons for stainless-steel-clad bundles.

Some sparking was observed during shearing of the Zircaloy-2 tubes, but there was no evidence of oxygen contamination on particles in the following sizes: $>\frac{3}{8}$ in. (>9520 μ), 149 to 297 μ, and 74 to 149 μ. There was considerable cracking of the cladding, and the 44- to 74-μ and <44-μ size fractions contained 48 to 73% zirconium.

Attempts to shear intact, second-generation, 6- by 6-in. sheathed fuel assemblies containing "eggcrate" grids (such as the Consolidated Edison core B) were unsuccessful because the sheath prevented proper holding of the fuel. Currently, fuel disassembly is being studied in which (1) fuel tubes are pulled individually and then sheared in bundles; and (2) the fuel assembly is quartered by abrasive sawing after removing several rows of fuel tubes, and the quartered sections are sheared. In one test a force of 24 to 130 lb was required to pull or push one fuel tube from the assembly.

(D. M. Paige)

Dissolution of Zirconium-Clad Fuels

Dissolving of zirconium-clad zirconium-uranium alloy fuels is most readily accomplished in aqueous HF to which an oxidant may be added to increase the solubility of uranium in the solution. At the Savannah River Plant, it was desired to provide for the processing of such fuels [for example, the seed core of the Pressurized-Water Reactor (PWR) at Shippingport] in dissolvers constructed of type 309SCb stainless steel. Since such an alloy is much more compatible with HNO_3 than with HF, the use of combinations of these reagents was investigated. Because of the highly corrosive nature of HNO_3-HF mixtures, the dissolving studies were closely paralleled with corrosion tests. There are some advantages in the use of the two reagents in that the addition of HNO_3 suppresses the evolution of hydrogen, minimizes precipitation of UF_4 by oxidizing uranium to the soluble uranyl form, and dissolves the tin that is present if Zircaloy cladding is used.

Occhipinti and Owen[5] have recently reported the results of studies leading to a feasible dis-

Fig. II-1 Comparison of particle-size fractions produced from shearing Zircaloy-2- and stainless-steel-clad UO_2 prototype fuel assemblies.[1]

solution procedure. As shown in Fig. II-2, the rate of dissolution of zirconium and Zircaloy-2 is almost linearly dependent on the HF concentration, is moderately slowed by reducing the temperature, and is only slightly increased by increasing the HNO_3 concentration. This suggested that dissolver corrosion would be minimized by the use of dilute HNO_3 containing the minimum amount of HF needed to dissolve the zirconium (5 moles of HF per mole of zirconium). Corrosion studies with type 309SCb stainless steel, some of which are summarized in Fig. II-3, indicated that corrosion rate was also very dependent on HF concentration, although somewhat more dependent on temperature and HNO_3 concentration than was the zirconium dissolution rate.

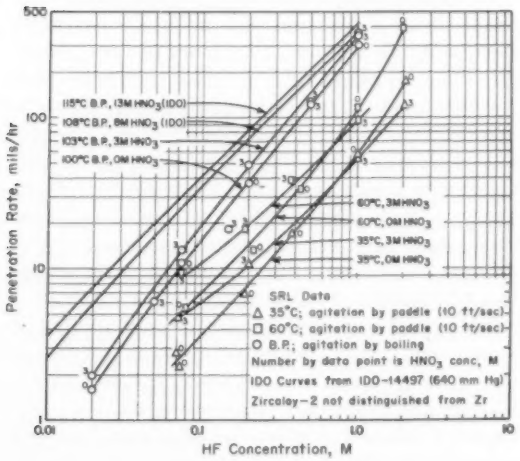


Fig. II-2 Dissolution rates of zirconium and Zircaloy-2 in HF-HNO_3, with HF concentration as continuous variable.

Examination of both Zircaloy-2 dissolution and type 309SCb stainless-steel-corrosion data, shown in Fig. II-4, indicated the advantages of dissolution at lower temperatures since the corrosion rate decreases more rapidly than the dissolution rate as the temperature is lowered. It was also found that dissolution could be carried out at 60°C or lower by continuously feeding concentrated (30*M*) HF to 1.0*M* HNO_3 in the dissolver through a Hastelloy F line extending below the liquid level. Agitation is necessary since the operation is conducted below the boiling point. The HF is added at a uniform rate throughout the dissolution period, the rate being limited by heat removal and off-gas capacity. Clear and stable dissolver solutions were prepared containing about 0.5*M* zirconium, 0.4*M* nitrate, and 2.5*M* fluoride.

Since the ratio between dissolution rate and corrosion rate at a given temperature does not change with changes in HF concentration, the

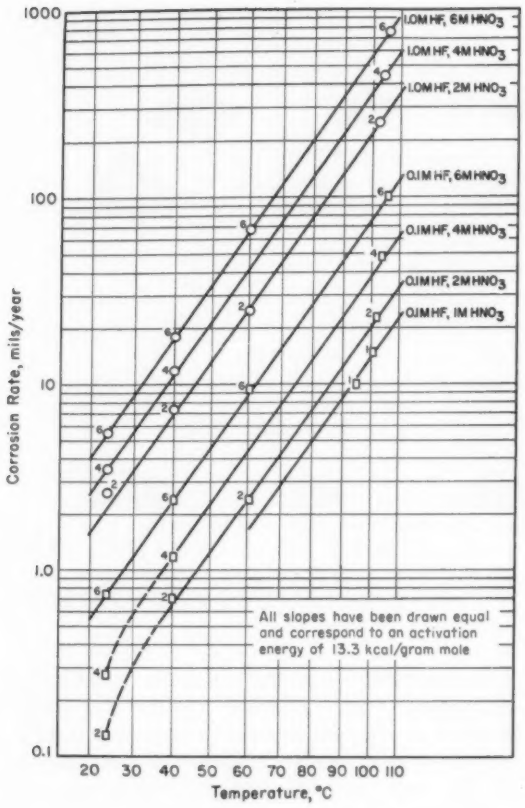

1.0M HF, 6M HNO3
1.0M HF, 4M HNO3
1.0M HF, 2M HNO3
0.1M HF, 6M HNO3
0.1M HF, 4M HNO3
0.1M HF, 2M HNO3
0.1M HF, 1M HNO3
All slopes have been drawn equal and correspond to an activation energy of 13.3 kcal/gram mole
Corrosion Rate, mils/year
Temperature, °C
1000
100
10
1.0
0.1
20 30 40 50 60 70 80 90 100 110

Fig. II-3 Corrosion rate of 309SCb stainless steel in HF-HNO_3, with temperature as continuous variable.[5]

amount of vessel corrosion remains proportional to the thickness of Zircaloy penetrated and thus to the number of charges dissolved. It was computed that at 70°C 10 tons of zirconium alloy plates could be dissolved in successive charges over a period of two to three weeks with less than 1 mil of vessel corrosion. Downstream from the dissolver, solutions may be processed in type 304L stainless-steel equipment. For corrosion control, $Al(NO_3)_3$ is added to complex the free fluoride remaining after zirconium dissolution.

In work at the Idaho Chemical Processing Plant (ICPP),[6] the processing of a late type of seed fuel for the Shippingport PWR has recently been investigated. This fuel consists of compacts of ZrO_2 and UO_2 clad with Zircaloy in typical plate configuration. The compacts contain 28 wt.% UO_2 and comprise about 22 wt.% of the fuel element.

Although decladding is easily accomplished with dilute HF, the rate of attack on ZrO_2 by this reagent is only about one-thousandth of that on the metal. More concentrated (20*M*) HF does attack the ZrO_2-UO_2 at a usable rate, but, because of solubility, only low concentrations of zirconium are possible. The insoluble UF_4 formed can be dissolved by oxidation with 0.1*M* chromic acid.

On the basis of these observations, a three-step dissolution process is proposed for this material:

1. Decladding in 5*M* HF at 50 to 60°C. The decladding waste solution is decanted from the heavy compacts remaining in the dissolver.
2. Zirconia dissolution in boiling 20*M* HF. This ZrF_4 waste solution is decanted from insoluble uranium tetrafluoride. A low concentration of KF may be used to suppress uranium solubility.
3. Dissolution of UF_4 in boiling 0.1*M* chromic acid, followed by addition of $Al(NO_3)_3$ to a concentration of 1.1*M* to provide a solvent-extraction feed solution.

For the most part, equipment constructed of Monel metal can be used for the dissolution process. Waste solutions can be readily concentrated and are amenable to calcination as a means of producing a solid waste.

Dissolution of Sintered Aluminum Powder (SAP)

In organic-cooled reactor technology, use is made of an aluminum-base metal composition, designated as sintered aluminum powder (SAP), for cladding UO_2 pellets. This material is a powder-metallurgy product containing both aluminum and Al_2O_3. It exhibits adequate strength at temperatures compatible with the limitations of organic coolants and has a low neutron cross section. Fuel elements using SAP have been considered for the Italian organic-cooled test reactor known as PRO (although they are no longer planned for this reactor), as well as for other organic-cooled reactors. Some studies on dissolution of the cladding for this fuel have recently been reported by Beone.[7] The behavior of SAP in the mercury-catalyzed HNO_3 normally used for dissolving aluminum-clad and aluminum alloy fuels differs markedly from that of aluminum. Reaction rates of SAP are very low, and the dissolution time required is almost unacceptable for plant application. Settling rates

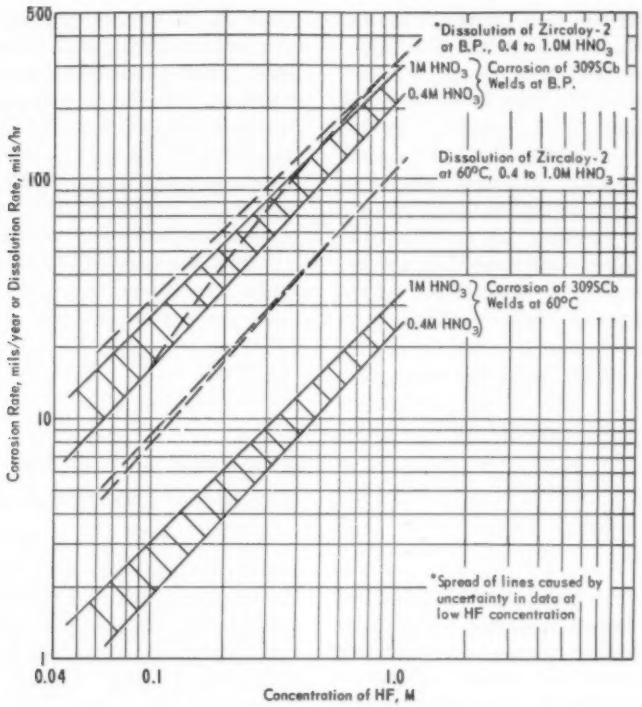


Fig. II-4 Dissolution of Zircaloy-2 and corrosion of 309SCb stainless-steel welds in HF-HNO_3 (Ref. 5).

of suspended Al_2O_3 are, however, very favorable for removal of the Al_2O_3 from the process stream, and recovery of uranium should be very feasible by standard processes.

Dissolution of Refractory Oxides

Refractory oxides of uranium, plutonium, and thorium, and mixtures of these, are of major importance as power-reactor fuels. Little aqueous processing of such materials has been done as yet. Unirradiated UO_2 dissolves readily in HNO_3, but the corresponding oxides of plutonium and thorium may require the addition of fluoride to achieve ready dissolution. As the firing temperature in preparing these fuels is increased, and/or as the burnup and temperature of irradiation are increased, the difficulties of rapidly and completely dissolving them increase correspondingly.

A study is under way at ORNL[1] to determine the effect of density and manufacturing conditions on the dissolution characteristics of pellets of high-fired UO_2 and PuO_2 and their mixtures in HNO_3 and HNO_3-HF mixtures. It was found that roughening of UO_2 pellet surfaces during dissolution resulted in dissolution in about one-third of the time predicted from the initial dissolution rate, because of increased surface area. The dissolution rate of PuO_2-UO_2 pellets fabricated commercially depended on the percentage of PuO_2 present and the method of fabrication. The time required for dissolution of 1600°C-fired coprecipitated pellets in 10*M* HNO_3 increased from 1 to 7.5 hr as the PuO_2 content increased from 0.5 to 35%. Pellets produced by coprecipitation required about three times as long for dissolution as mechanically blended pellets.

Cleveland[8] notes that PuO_2 prepared by burning plutonium in air dissolves quite slowly in HNO_3 and in HCl, less than 1% dissolving in 1 hr in boiling 16*M* and 12*M* acid, respectively. Hydrobromic acid is a much better solvent since 9.4% was dissolved in 1 hr in boiling 9*M* acid. More than 3 kg of PuO_2 was dissolved in successive batches that were refluxed 6 to 8 hr with 9*M* HBr. The fresh portions of oxide and acid

were added to the filtered residue left from the preceding dissolution. Less than 0.5 g of plutonium remained in the final residue.

In other work at ORNL,[1] the dissolution of ThO_2–4% UO_2 solid solutions (prepared by the sol-gel process) in 13*M* HNO_3 containing small concentrations of HF and $Al(NO_3)_3$ has been studied. Many hours are required for complete dissolution to concentrations approaching 1*M* thorium. Heel type dissolution procedures were investigated in which fresh 13*M* HNO_3–0.04*M* HF–0.04*M* $Al(NO_3)_3$ and ThO_2–4% UO_2 were added to the solid residue from a preceding batch and boiled for 20 hr. At steady state, 87% of the oxide initially present in each cycle was dissolved, yielding solutions that were 0.8*M* in thorium and 0.5*M* in H^+.

Treatment of Carbide and Graphite Fuels

A variety of methods has been proposed for the recovery of enriched uranium from fuels consisting of graphite that has been impregnated with $UO_2(NO_3)_2$ solutions and baked to decompose the salt (e.g., fuel for the Ultra High-Temperature Reactor Experiment, UHTREX, formerly known as the Turret reactor). The techniques have included (1) grinding and acid leaching, (2) combustion of the graphite followed by leaching or volatilization of uranium from the ash, and (3) chemical or electrochemical attack on the graphite matrix. In work at the ICPP,[9] it has been observed that the graphite must be ground to <200-mesh particles in order to recover at least 99% of the uranium by leaching with HNO_3. Only 43% was recovered from particles coarser than 100 mesh. It was also found that the graphite is disintegrated readily by electrolysis at 82°C in 16.5*M* HNO_3 at a current density of 0.16 amp/cm^2. A large fraction of the uranium was not dissolved, however, and the residue contained many spherical particles 80 to 220 μ in diameter. Shimokawa[10] also noted the successful electrolytic disintegration of irradiated UO_2-graphite pellets.

Carbides of uranium and thorium will be used as fuel in the sodium-cooled Hallam reactor and in the High-Temperature Gas-Cooled Reactor being built at Peach Bottom, Pa. A low-temperature water hydrolysis process was developed at ORNL[11] as a means of preparing these fuels for solvent-extraction recovery. It was found that irradiation sharply inhibits the water hydrolysis of uranium carbide.[11] More recently, specimens of UC irradiated to 6000 and 16,000 Mwd/metric ton were found to be inert to water at 80 and 100°C in 24-hr exposure tests.[1] Specimens irradiated to only 600 Mwd/ton hydrolyzed completely but more slowly than unirradiated specimens. Pyrohydrolysis of irradiated specimens with steam at 750°C formed UO_2 virtually free of carbon, and the UO_2 could be dissolved in HNO_3 for extraction. If dissolution of the carbide directly in 60% HNO_3 is attempted, about half the carbide carbon remains in solution as HNO_3-soluble organic compounds. These must be destroyed by strong oxidants prior to solvent extraction.

Processing of Fuel from Organic-Moderated Reactor Experiment

Typical fuel assemblies for the Organic-Moderated Reactor Experiment (OMRE) consist of a group of parallel stainless-steel-clad plates of UO_2 dispersed in stainless steel. The core of the plates is prepared by powder-metallurgy techniques. When exposed to the hot terphenyl coolant in the reactor, the plates acquire a coating of a thin (0.1 to 1.0 mil), hard film of organic material representing a carbonaceous degradation product of the coolant together with some inorganic material. When the first core from this reactor was processed at the ICPP, it was considered necessary to remove this film prior to dissolution in H_2SO_4 so as to prevent interference by suspended film particles with subsequent process steps such as solvent extraction.[12]

Decker and Jacobson[13] have recently reviewed and reinvestigated this problem. It had previously been found that (1) the material originally used for film removal (Turco 4502, a commercial basic permanganate metal-cleaning preparation) would not consistently remove the dark film from plates cut from second-core fuel assemblies, particularly if a heavy deposit was present; and (2) the hard film coating could be removed by heating in air to 500°C, but this was not considered to be an appropriate plant procedure. Hot-cell tests have now been made in which fuel samples were dissolved either chemically in 6.5*M* H_2SO_4, followed by addition of HNO_3 to dissolve UO_2, or electrolytically in 8*M* nitric acid. Dissolution by either process was equally rapid for both coated and uncoated fuel surfaces. Finely divided solids that were present in the

solutions coalesced rapidly after agitation with tributyl phosphate–kerosene mixtures. The solution from electrolytic dissolution was solvent extracted without difficulty, and it was observed that all the solids remained in the aqueous raffinate and did not accompany the uranium. As a result of this work, it was concluded that the coating present on irradiated OMRE fuel assemblies should not be considered a hindrance to processing and that its removal is unnecessary.

Solvent Extraction Processing

Solvent Deterioration

In the use of tributyl phosphate (TBP)–hydrocarbon diluent mixtures for the solvent extraction of solutions of irradiated fuel, it is observed that dibutyl phosphate (DBP) is produced from TBP by dealkylation due to irradiation.[14] This is undesirable because DBP forms stable complexes with fission-product zirconium which are soluble in the organic phase, and, if the concentration of DBP is sufficiently high, insoluble compounds, including compounds of uranium, may be formed in the process streams. These effects result in poor decontamination and product losses.

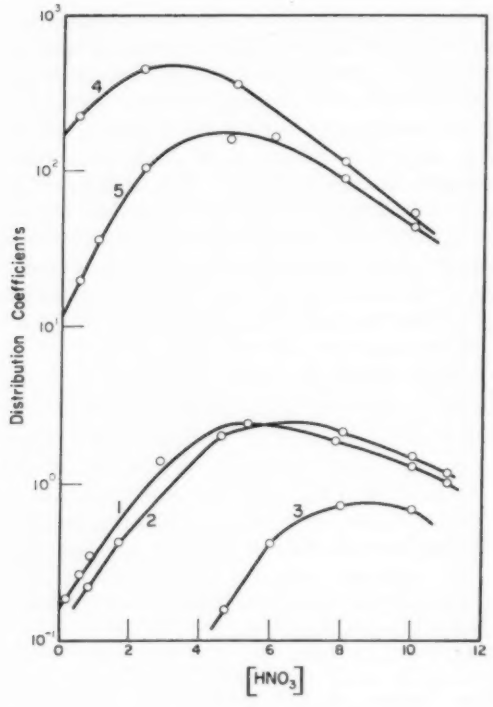
It has been proposed to improve the radiation resistance of phosphorus-derived extractants by introducing a phenyl group adjacent to the phosphoryl group in the molecule. An example is the substitution of di-*sec*-butyl phenyl phosphonate for TBP.[15] Lane and Pilbeam[16] have recently prepared and tested three additional compounds: diethylphenylphosphonate, diphenylmethylphosphine oxide, and diphenyloctylphosphine oxide. They were particularly concerned with evaluating the effects of free radicals produced by initial decomposition of the aqueous phase; for example, the formation of phenolic compounds from free hydroxyl radicals. It was conceived that this would adversely affect the performance of such compounds as extractants by producing a molecule capable of retaining metals by chelation.

The performance of these compounds was tested by irradiating them to 10^8 rads while they were diluted with hydrocarbons and in contact with $3M$ nitric acid. It was necessary to use an aromatic diluent because of the limited solubility of the compounds in odorless kerosene. In all three cases the irradiation produced an unidentified species that strongly retained hafnium (used to simulate the behavior of zirconium). In other work certain phenyl-substituted phosphine oxides containing a phenolic hydroxyl group ortho to the P–O bond were shown to complex hafnium. Similar behavior was observed for phenyl-substituted phosphine oxides in contact with nitric acid. From these results it was recommended that new neutral organic phosphorus extractants for fuel processing should not contain phenyl groups adjacent to the phosphoryl group.

In this connection it is of interest to note a recent patent[17] in which the treatment of used TBP process solvent by agitation with a warm slurry of 1 to 10% $Mg(OH)_2$ in 0.5 to $2M$ NaOH is covered. It is indicated that this treatment is superior to caustic-permanganate treatment in reducing the retention of zirconium and niobium by the solvent, and that mono- and di-alkyl phosphates and degraded diluent are removed without removing the TBP.

New Types of Extractants

High-molecular-weight amines and quaternary ammonium compounds, principally those containing long aliphatic chains, are good extractants for uranium and plutonium. Separation processes based on the use of such compounds have been devised and applied.[18] Consideration has been given to a variety of basic nitrogen compounds as extractants. Kennedy and Perkins[19] have studied the extraction of uranyl ion and tetravalent plutonium from HNO_3 solutions by the oxide of a tertiary amine. The oxide was prepared by reaction of hydrogen peroxide with Alamine 336 — a commercial mixture consisting mainly of long chain (C_8–C_{10}) tertiary amines. In one series of tests, distribution coefficients were compared as a function of HNO_3 concentration (0 to $11M$) with solutions containing 15% of either Alamine 336 or its oxide in dibutyl carbitol. Curves 1 and 2 of Fig. II-5 show that the extraction of uranyl ion by both compounds is very similar. Curves 4 and 5 show that the distribution coefficients for tetravalent plutonium at low acidity are almost an order of magnitude smaller with the amine oxide than with the tertiary amine but that the coefficients approach each other at high acidity. The report[19] also gives data relating distribution coefficients to concentration of amine oxide in the diluent.



Curve	Ion and extractant
1	UO_2^{2+}, 15% Alamine 336/dibutyl carbitol
2	UO_2^{2+}, 15% Alamine oxide/dibutyl carbitol
3	UO_2^{2+}, dibutyl carbitol
4	Pu^{4+}, 15% Alamine 336/dibutyl carbitol
5	Pu^{4+}, 15% Alamine oxide/dibutyl carbitol

Fig. II-5 Distribution coefficients vs. HNO_3 concentration.[19] *(Courtesy of* Journal of Inorganic and Nuclear Chemistry.)

Polish authors[20] have reported work on extraction by phenoxyethylamines. The compounds used were β-phenoxyethylamine and β-(2-methylphenoxy)-ethylamine dissolved in either benzene or *o*-chlorobenzaldehyde. The effects of *p*H (0 to 3) on extraction in chloride and nitrate systems were studied. It was found possible to separate uranium from protactinium and thorium using both reagents.

Symposium on Neptunium-237 and Plutonium-238 Production

The U. S. program for the production of ^{237}Np and ^{238}Pu, which is aimed at providing sufficient quantities of the latter for use in certain types of energy sources for space vehicles, was discussed in a symposium sponsored by the American Chemical Society which was held in January 1964 at Denver, Colo. This symposium was reviewed earlier[21] and has now been published,[22] with the exception of one paper on potassium plutonium sulfate. (C. E. Stevenson)

Plant and Equipment Design and Operation

With the high burnup now expected in reactor fuels, it becomes very important to have high-performance solvent-extraction contactors that, by minimizing contact time, minimize radiation damage to solvents. Two such contactors developed in the United Kingdom, a mixer-settler and a pulsed plate column, were described in the

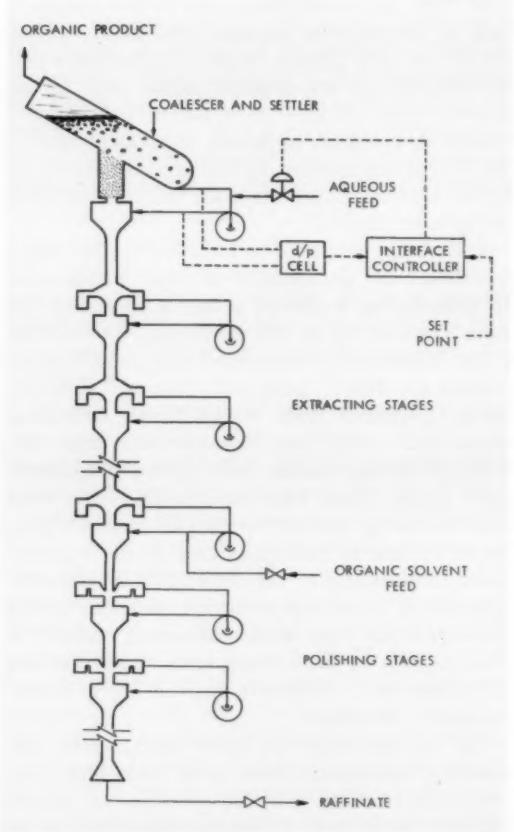


Fig. II-6 Stacked-clone-contactor cascade.[26]

preceding Review.[23] Work with hydroclone contactors has also been reviewed previously.

Stacked-Clone Contactors

A recent report by Whatley and Woods[26] documents work at ORNL on high-performance stacked-clone contactors. The authors state that they now believe that hydroclone contactor development is at a point where basic principles have been proved and the probability is high for useful application to nuclear fuel processing. This report was written to present available information on basic principles and operational characteristics and thus allow consideration of where the contactor would be useful.

Construction details are presented for the Mark X contactor. A variety of basic shapes were studied in developing the proposed design. The evolution of the design was based on observed trends and intuition. Theory and previous technology were of little assistance, and many apparently anomalous effects were noted. The criteria for good configurations were throughput, holdup volume, and stage efficiency. Standard stainless-steel centrifugal pumps were used.

In the development work most of the data were taken using four stages in countercurrent cascade plus three polishing stages below the stage into which the light (organic) phase was fed. [The polishing stages are used to deentrain the light phase from the heavy (aqueous) phase.] The bottom polishing stage discharged its underflow into the apex of a conical chamber. The settling section at the organic discharge consisted of a packed section discharging into an inclined settler. The interface level was controlled by controlling the feed rate at the aqueous inlet. Figure II-6 illustrates the arrangement used, although in practice the unit was operated horizontally.

The experimental program has established principles of a workable design using three chemical systems: benzoic acid distributed between water and Supersol, benzoic acid distributed between water and Amsco, and $UO_2(NO_3)_2$ distributed between 1*M* sodium nitrate and 18% TBP in Amsco. Variables studied included shape, volume, and length of the clone body; the shape and volume of the underflow chamber; the relative sizes of the feed ports and vortex finders; and the dimensions of the gap through which the recirculating pump draws suction.

Factors affecting capacity, stage efficiency, holdup times, entrainment, and control are discussed. Figure II-7 shows some of the flooding data obtained with the Mark X contactor. Holdup times in the experimental model were shown to be less than 4.5 sec per theoretical stage vs.

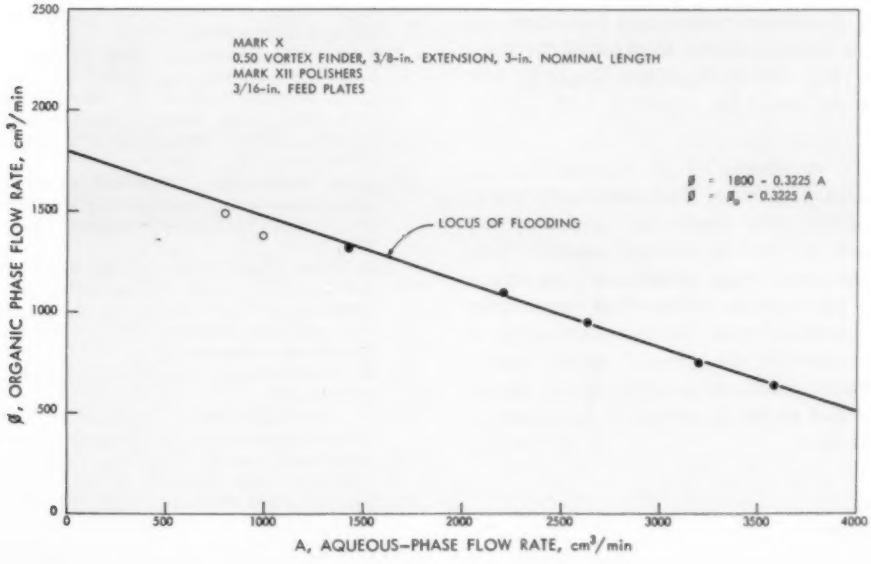


Fig. II-7 Effect of relative flow rates on flooding in the stacked-clone contactor.[26]

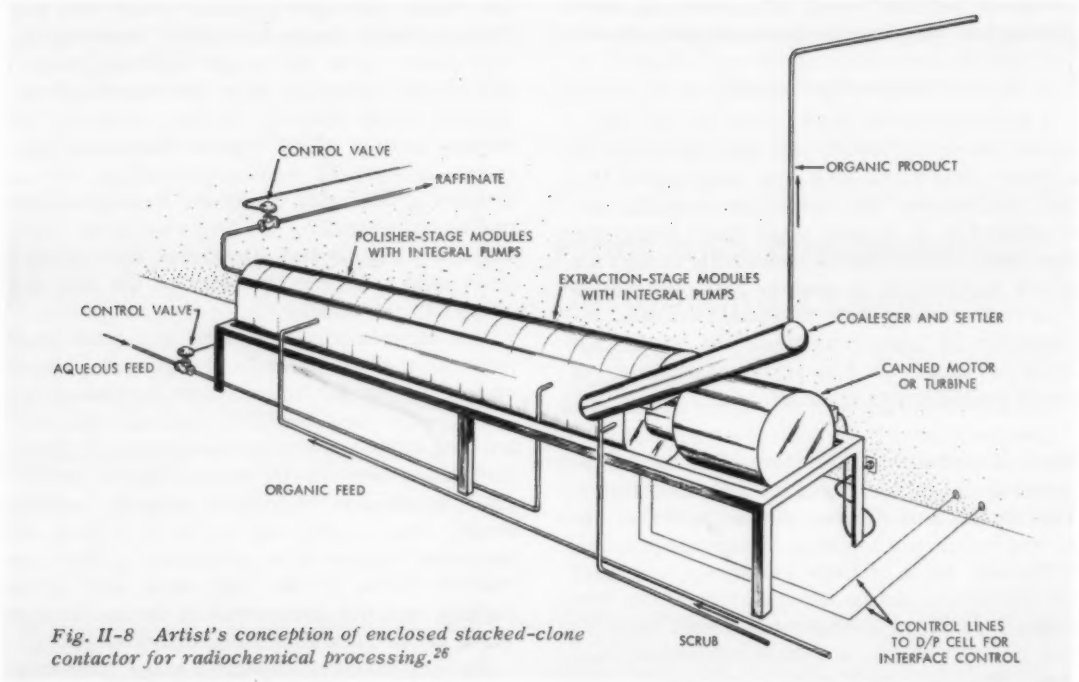


Fig. II-8 Artist's conception of enclosed stacked-clone contactor for radiochemical processing.[26]

the 30 sec in pulsed columns or mixer-settlers using Purex flow sheets. It is pointed out that there would probably be more holdup in pipelines than in the contactor. Entrainment of the light phase was shown to be about 3.5% in the absence of polishing stages and less than 1% with three polishing stages. Control of the contactor was very satisfactory and response was very rapid, as would be expected with the low holdups.

A concept is presented of a contactor for radiochemical plant use. The pump body would be built into the clone cavity, and, probably, all stages would be run by a single motor. Construction material would presumably be stainless steel. The authors believe that manifolded clones in parallel would be more effective in increasing capacity than would larger single clones, although there is no evidence for this as yet. Figure II-8 shows an artists's conception of such a contactor. (D. M. Paige)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Various types of processes based on the volatilities of uranium and plutonium hexafluorides have been proposed for the processing of irradiated reactor fuels. Volatility processes are being applied to both fully enriched fuels and low-enriched ceramic fuels. In these processes spent reactor fuels are converted to fluorides, and decontamination is carried out by distillation or absorption-desorption methods. Since the concentration of uranium in fully enriched fuel is low, the initial step of the processing scheme involves the separation of uranium from the fuel matrix before its recovery by volatility methods. A significant feature of several volatility processes under development for both high- and low-enriched fuels is the application of fluidization techniques to direct chemical conversion of fuel materials into gaseous compounds. Alternative processes for the recovery of uranium from alloy fuels are the Nitrofluor and the fused-salt volatility processes.

A comprehensive survey of U. S. work since 1958 on fluoride-volatility separations processes was presented at the 1964 Geneva Conference.[1] This paper covered work being carried out at Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL), and Brookhaven National Laboratory (BNL). Jacobs[2] has compiled an annotated bibliography of selected literature on the processing of irradiated reactor fuel and breeding materials which updates a previous bibliography issued in 1958.

Nitrofluor Process

The Nitrofluor process for treating spent reactor fuels is based on fuel dissolution, or disintegration, in anhydrous HF solutions containing complexing agents in the form of N_2O_4 or N_2O_3, with or without NOF. Uranium and plutonium, which readily dissolve in the solvent, are recovered from fission products and cladding materials by volatility techniques. Recent work at BNL[3] has been concerned with the study of the kinetics of dissolution of uranium-zirconium and uranium-aluminum alloys in Nitrofluor solvents. The solvents that have been evaluated are a ternary azeotrope containing NOF, N_2O_3, and HF which boils at 95°C and a binary azeotrope that has an approximate composition $N_2O_3 \cdot 12.6HF$ and boils at 68°C. As the reaction progressed, the dissolution rate decreased markedly, primarily due to depletion of the oxidant in the solvent. A high average reaction rate was achieved by providing a solvent-to-metal weight ratio of 10 or higher. The reactivity of both solvents for dissolving zirconium alloys at 60°C was nearly identical. When a solvent-to-metal weight ratio of 10 was used, Zircaloy dissolved in 3 hr in the ternary solvent at 60°C. For a similar rate to be achieved with aluminum, a temperature of 121°C was required. Preliminary tests have shown significantly less reactivity of the binary azeotrope than of the ternary azeotrope toward aluminum. The dissolution rate of aluminum in $N_2O_3 \cdot 12.6HF$ can be improved by adding N_2O_3 to the system to achieve the composition N_2O_3-8.3HF.

A series of tests was performed[3] with an aluminum-uranium alloy fuel to demonstrate the recovery of uranium by volatilization of UF_6. A simulated alloy fuel was dissolved in the ternary azeotrope, and the excess solvent was evaporated. A solid residue containing complex salts of uranium and aluminum was left. A single 30-min treatment of the residue with liquid BrF_3 at 150°C was sufficient to volatilize 99% of the uranium as UF_6. On the basis of these results, it appears that separation of

aluminum from the residue before the uranium recovery step is not required.

Volatility Processes for High-Enriched Fuels

In the processing of reactor fuels containing highly enriched uranium, the initial step of the process involves the separation of uranium from the fuel matrix; this frees the uranium for subsequent recovery by fluoride-volatility techniques. Several processes that involve separation methods based on the relative volatility of chlorides are being developed. Studies are currently being made on zirconium-uranium and aluminum-uranium alloy fuels. Uranium is separated from the alloy initially by conversion of the alloying metal to a volatile chloride. Final recovery of uranium is achieved by fluorination to produce volatile UF_6. Volatility processes are also being applied to graphite-matrix reactor fuels containing enriched uranium carbide.

URANIUM-ALLOY FUELS

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is being developed at ANL.[4,5] The process uses three principal steps in which chemical separation of the various fuel constituents is achieved by selective volatilization of chlorides and fluorides. The initial step involves the separation of the alloying and cladding material (aluminum or zirconium) from uranium by reaction at approximately 350°C with hydrogen chloride gas while the fuel element is submerged in a fluidized bed of inert alumina particles. Separation of the alloying and cladding elements occurs by formation of volatile $ZrCl_4$ and $AlCl_3$. Uranium is converted to solid UCl_3 during hydrochlorination and, for the most part, remains associated with the fluid-bed material. A portion of the UCl_3 is entrained in the gas stream leaving the reactor, and therefore a packed-bed high-temperature gas filter is employed in series with the fluid-bed reactor to ensure adequate retention of uranium within the system.

In the second step the UCl_3 in the fluid-bed reactor and packed-bed filter is converted to UF_4 by reaction with HF gas. This process step has been adopted to avoid the production of gaseous chlorine and chlorine fluorides in the direct fluorination of UCl_3. Recovery of uranium as UF_6 is achieved in the third step by the reaction between UF_4 and fluorine at 250 to 500°C.

Ramaswami, Levitz, and Jonke[4] have reported the results of process studies performed in a 1½-in.-diameter fluid-bed reactor on the recovery of uranium from aluminum and zirconium alloy fuels. The primary aim of the bench-scale studies was to establish processing conditions that would result in a minimal amount of unrecoverable uranium. Uranium losses are primarily due to (1) passage of uranium through the packed-bed filter during the hydrochlorination step, either as a volatile chloride or as a particulate solid, and (2) retention of uranium by the alumina in the fluid bed and filter bed at the end of the three-step reaction sequence. The bench-scale tests show that uranium recoveries of greater than 99% can be consistently achieved under a wide variety of process conditions. The operating conditions that were found suitable for processing uranium–Zircaloy-2 alloy fuel are as follows:

Bed Material
- High-fired alumina (fused or sintered)
- Fluid bed, sufficient quantity of nominal 40-mesh alumina to cover the element (a multiplate assembly)
- Packed-bed filter, –14 +20-mesh alumina, 6-in. bed depth

Hydrochlorination
- Temperature of fluid bed, 350 to 450°C
- Temperature of packed-bed filter, 330 to 350°C
- Time, approximately 8 hr per charge
- Gas velocity, 0.5 to 0.7 ft/sec in the fluid bed and packed-bed filter
- Quantity of hydrogen chloride, approximately 2.5 stoichiometric amounts
- Concentration of hydrogen chloride, 5 to 75 vol.%, as required to maintain high reaction rates

Hydrofluorination
- Temperature of fluid bed and packed bed, 270 to 350°C
- Time, 1 hr
- Hydrogen fluoride concentration, 20 to 50 vol.% in nitrogen

Fluorination
- Gradual increase in temperature from 250 to 500°C while fluidizing with 5 to 10 vol.% fluorine in nitrogen, followed by gradual increase in fluorine concentration to 90 vol.% at 500°C
- Total fluorination time, about 4 to 8 hr depending upon the quantity of uranium in the charge

For processing aluminum-uranium alloys, an 8- to 12-in.-deep bed of alumina must be provided in the packed-bed filter to assure low uranium loss during hydrochlorination. The recommended temperatures during the hydrochlorination step are 200 to 400°C in the fluid-

bed reactor and 180 to 200°C for the packed-bed filter.

Holmes and Barghusen[5] have described the pilot-plant facility constructed at ANL to demonstrate the processing of multiplate assemblies of zirconium-uranium or aluminum-uranium alloy fuel. A schematic diagram of the facility and a description of the process equipment were published in the previous issue of *Reactor Fuel Processing*.[6] Completely satisfactory performance of the pilot-plant equipment has been achieved in tests with charges up to 20 kg for zirconium-uranium alloy and up to 14 kg for aluminum-uranium alloy. When fluid-bed techniques were used, complete control of highly exothermic reactions was demonstrated at high processing rates. Recent results[7] have shown that 99% of the uranium in an aluminum-uranium alloy assembly can be recovered as UF_6 by employing a two-temperature fluorination procedure. The fluorination procedure involved introducing dilute fluorine (6 vol.% fluorine in nitrogen) into a fluidized reactor bed at 250°C and then slowly raising the temperature of the bed to 500°C over a 2- to 6-hr period. Fluorination was completed by operating with 30 to 60 vol.% fluorine under static bed conditions for an additional 2 hr at 500°C.

GRAPHITE-MATRIX FUELS

Engineering-scale investigations on methods for processing graphite reactor fuels are being conducted at ORNL. Blanco et al.[8] at ORNL have discussed both aqueous and nonaqueous processing methods for fuel materials containing uranium carbide in a graphite matrix. The initial step in the processing of graphite-matrix fuel is burning it in oxygen to convert the graphite to CO and CO_2 and to convert uranium, thorium, and other materials to their respective oxides. The nonvolatile oxide ash is then treated by aqueous-dissolution, fluoride-volatility, or chloride-volatility methods.[8] Detailed descriptions of development work on the oxidation-fluorination process have been presented in previous issues of *Reactor Fuel Processing*.[9,10]

In order to predict the effects of operating variables in large-scale processing operations, Scott[11] has prepared a mathematical model for the analysis of the burning of graphite-uranium fuel materials in fixed and moving beds. The results of the analysis compare favorably with experimental data obtained at ORNL. Several potential operational problems were revealed, such as high carbon monoxide content and excessive heating of the fuel during combustion. On the basis of the analysis, safe operating conditions were predicted for burning of deep beds of fuel in tubular and annular reactors. The conditions were a maximum temperature less than 1300°C, a maximum wall heat flux less than 7.5 cal/(cm^2)(sec), and a maximum carbon monoxide concentration less than 12.5 vol.%.

It is planned that a single vessel be employed during the oxidation-fluorination steps in the processing of graphite-matrix fuels. Several candidate construction materials have been evaluated in a series of corrosion tests simulating the environments in the oxidation-fluorination cycle.[12] Coupons of high-nickel-content alloys (Duranickel, Inconel, Inconel X, Monel, L-nickel, INOR-8, and HyMu 80) were exposed to the oxidation-fluorination cycle according to the following schedule: (1) 1 hr at 700°C in a 5 vol.% CO–65 vol.% CO_2–30 vol.% O_2 mixture; (2) 1 hr in helium as the temperature is reduced to 400°C; (3) 1 hr in fluorine at 400°C; (4) 1 hr in helium as the temperature is raised to 700°C. Of the alloys investigated INOR-8, Duranickel, and L-nickel appear to be the most durable construction materials for the oxidation-fluorination process. In tests with exposures of 20 to 40 cycles, these materials showed corrosion rates less than 15 mils/month. In general, all materials other than INOR-8 were subject to some intergranular attack or to selective leaching. On the basis of this observation, INOR-8 appears to be the optimum construction material.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

Several processes that involve separations based on the volatility of uranium halides are being developed for the processing of UO_2 fuel elements. A fluid-bed fluoride-volatility process is being developed at ANL[13] to recover uranium and plutonium from spent oxide fuel. In this process uranium and plutonium oxides are fluorinated with fluorine to produce volatile uranium and plutonium hexafluorides, which are subsequently decontaminated and separated from one another. A low-decontamination process for UO_2 fuels based on the volatility of uranium chlorides is being developed at ORNL.[14] Of major concern in the development of volatility

processes for low-enriched fuels is defining the behavior of plutonium during the separation steps and establishing methods for the recovery of plutonium.

CHLORINATION OF URANIUM DIOXIDE

Workers at ORNL[14] are investigating a decontamination process based on the reaction of UO_2 fuels with gaseous Cl_2-CCl_4 mixtures to produce volatile UCl_5-UCl_6. Goode[15] has reported the results of a series of tests investigating the separation and recovery of uranium and plutonium from fission products by chloride volatility. The process involves the initial conversion of UO_2 to U_3O_8 by heating it in oxygen at temperatures from 500 to 800°C, followed by chlorination at 500°C with 85 vol.% Cl_2–15 vol.% CCl_4. The volatile uranium chlorides produced, UCl_5 and UCl_6, were purified and decontaminated by fractional distillation and sublimation. Uranium recovery varied from 90 to 98% in 10 tests. The losses were attributed to incomplete chlorination-sublimation of uranium chlorides during the purification step. Volatilization of the plutonium was accomplished by the use of a large excess of the chlorinating reagent. It was observed that a large portion of the plutonium accompanied the uranium during the uranium-purification step. The distribution of plutonium throughout the process equipment was not that which would be expected from plutonium chloride volatility data. This behavior has been attributed to entrainment of plutonium with the uranium chlorides and physical adsorption on the surface of the equipment. The overall gamma decontamination factors for uranium were generally low (<50), with cesium, zirconium, niobium, and ruthenium being decontaminated least.

Gens and Atta[16] have considered that the decontamination of volatile uranium chlorides might be significantly increased by selective reduction to less volatile uranium compounds. Thermodynamic calculations were made to determine whether or not the reduction of volatile uranium chlorides to nonvolatile UCl_3 with CO is feasible. The reduction of gaseous UCl_5 and UCl_6 to UCl_3 with CO was found to be much less favorable thermodynamically than the reduction of gaseous UCl_4 to UCl_3. The calculations indicated that the yield of UCl_3 from the reaction of gaseous UCl_4 and CO would become very low if the temperature was increased to the point where large amounts of UCl_4 are vaporized. It was concluded that the reduction of gaseous UCl_4 with CO to produce solid UCl_3 in useful amounts does not appear feasible.

RECOVERY OF PLUTONIUM FROM URANIUM DIOXIDE FUEL

In the fluid-bed fluoride-volatility process being developed at ANL, declad fuel elements are reacted with oxygen and then with fluorine at about 500°C to convert the oxides to volatile UF_6 and PuF_6. The progress of engineering development work at ANL on this process has been reviewed in recent issues of *Reactor Fuel Processing*.[17,18] Supporting laboratory-scale investigations[13] are aimed at defining the conditions that result in a high degree of removal of UF_6 and PuF_6 from the fluidized alumina bed during fluorination of U_3O_8-PuO_2 mixtures. Mixtures of U_3O_8 and PuO_2 are being used in these studies to simulate the product that is formed by the oxidation of UO_2-PuO_2 fuel pellets. The U_3O_8-PuO_2 powder, mixed with inert alumina particles, is fed into the fluid-bed reactor with the fluidizing nitrogen stream. Fluorine gas is introduced into the reactor just above the point at which the oxide powder enters, and the fluorination reaction occurs as they mix.

The effect of fission-product oxides in the U_3O_8-PuO_2 mixtures on the retention of uranium and plutonium on the alumina fluid bed was investigated recently.[13] The U_3O_8-PuO_2 mixtures contained about 84 wt.% uranium and 0.4 wt.% plutonium, and the fission products, when present, comprised about 0.9 wt.% of the mixture. Tests were performed in which the oxide mixture was fed into the fluid bed at 500°C and fluorinated simultaneously with 20 vol.% fluorine; this was followed by a 5-hr recycle-fluorination period at 500°C using 100% fluorine. The presence of fission-product oxides did not materially affect the residual uranium content in the alumina-bed material. In all cases the quantity of uranium retained on the alumina represented less than 1% of that fed to the reactor. However, the concentration of plutonium retained on the alumina increased from 0.033 wt.% in the absence of fission products to 0.057 wt.% when fission products were added to the feed. Since both these values represent a high residual plutonium content, a test was performed in which the oxide feed material was subjected to an extended fluorination treatment to improve plutonium recovery. The

oxide mixture containing fission products was fed to the bed at 450°C using 20 vol.% fluorine. This was followed by recycle fluorination with 100% fluorine for periods of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C. The residual plutonium concentration on the alumina at the end of the fluorination period was 0.007 wt.%, which is equivalent to 3% of the plutonium charged to the fluid-bed reactor. Results of preliminary tests indicate that this fraction of plutonium lost can be reduced if the alumina bed is reused for the fluorination of several batches of oxide feed. This concept is currently under further study at ANL.

STAINLESS-STEEL DECLADDING

Two methods are being investigated for decladding stainless-steel-clad UO_2 fuel elements: (1) oxidative decladding by reaction of UO_2 pellets with oxygen to produce U_3O_8, which forms as a very fine powder and readily separates from the cladding, and (2) the chemical destruction of the cladding by the high-temperature reaction with oxygen in the presence of metal-fluoride promoters or hydrogen fluoride.

Processing of power-reactor fuels by low-decontamination methods is being investigated at Atomics International.[13] One method under study for uranium dioxide fuels is based on oxidation of the fuel in air or oxygen to remove the fuel from the cladding as U_3O_8 powder and reduction of the higher oxide to UO_2 by hydrogen. Bodine and associates[13] have investigated the oxidative decladding process and have observed that the method appears feasible for decladding irradiated fuels. Optimum conditions for decladding were found to lie in the oxygen pressure range of 15 to 25 in. Hg abs. and in the temperature range of 440 to 515°C. Three-foot sections of unirradiated fuel rods were declad in 2 hr. The decladding rate was increased by puncturing the cladding at 1-in. intervals and by vibrating the fuel rod during the oxidation step. In tests performed on 8-in. sections of fuel rods irradiated to 21,000 Mwd/ton, decladding rates were essentially unaffected by the extent of irradiation and >99.9% of the UO_2 fuel was removed from the cladding.

Workers at BNL[3] have observed that stainless steel is severely attacked by reaction with oxygen at 700°C in a fluidized bed of alumina containing 3 wt.% FeF_3. A series of tests was performed to demonstrate decladding of fuel-element bundles constructed of nine tubes of type 348 stainless steel (21-mil wall thickness) containing UO_2 pellets. Considerable difficulty was encountered in reacting all the cladding material. Only 80 to 90% of the UO_2 was removed from the cladding in 14-hr oxidation periods.

Preliminary tests at ORNL have shown that high oxidation rates of stainless steel can be achieved with gaseous mixtures of HF and oxygen.[14] Maximum reaction rates at 650°C for type 304L stainless steel occurred at 40 mole % HF in oxygen (see Fig. III-1). The tests were performed by suspending cylindrical specimens (1 in. long by ¼ in. in diameter) in a 2-in.-diameter nickel reactor for 1 hr. The presence of moisture or an inert gas decreased the oxidation rate. The reaction products were Fe_2O_3 and Cr_2O_3 with <1% fluoride content. It has been suggested that HF destroys the passivity of the stainless steel by formation of CrF_3, which is immediately converted to oxide. This mechanism is in agreement with a thermodynamic evaluation and with the observation that the addition of H_2O decreases the reaction rate. In one test in which 40 mole % F_2 in oxygen was used in place of HF, almost total conversion of stainless steel to fluoride occurred, but the reaction rate was only 3 mils/hr. Preliminary corrosion data indicate that nickel might be a suitable construction material for HF-O_2 environments at temperatures up to 650°C; corrosion rates of 2 mils/month were observed for a 40 mole % HF–O_2 mixture at 650°C.

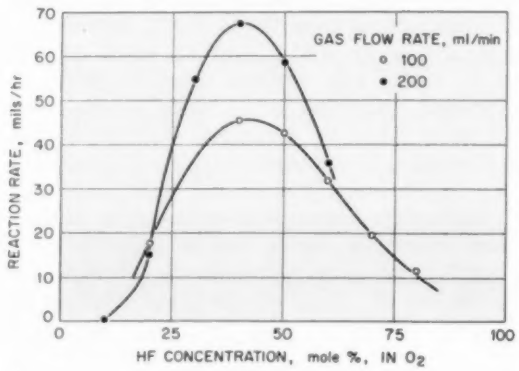


Fig. III-1 Variation of destructive oxidation rate for type 304L stainless steel with HF concentration in oxygen at 650°C (Ref. 14).

PROPERTIES OF PLUTONIUM HEXAFLUORIDE

The volatility of PuF_6 is utilized in the fluid-bed fluoride-volatility process to separate plutonium from most of the fission products. During the fluorination step and in subsequent operations, plutonium compounds are exposed to radiation from fission products. A study of the decomposition of PuF_6 by gamma radiation has been undertaken[13,20] to obtain information concerning the extent of decomposition, the products of the decomposition, and the fundamental processes involved in the radiation chemistry of PuF_6.

Plutonium hexafluoride exposed to fission-product gamma radiation decomposes to form PuF_4 and elemental fluorine. Under the conditions of the fluid-bed fluoride-volatility process, it is expected that the extent of decomposition will not represent a serious problem. The G value (number of molecules decomposed per 100 ev absorbed) for the decomposition of PuF_6 in the absence of added gases was determined to be 7.5 ± 1.7. Additions of helium lowered the G value only at high helium pressures, and this result was interpreted in terms of an enhancement of the back reaction by an activated helium species. A study of the effect of krypton on the decomposition of PuF_6 by gamma radiation revealed a marked enhancement (G value of 19 based on energy absorbed by PuF_6 alone) of the decomposition at an electron fraction of krypton of 0.73 and an exposure dose of 1×10^8 rads. No such enhancement was observed at an exposure dose of 2×10^8 rads. Addition of fluorine or oxygen to PuF_6 reduced the extent of decomposition of PuF_6 by gamma radiation. It was observed[20] that gamma irradiation of mixtures of PuF_4 and elemental fluorine produced PuF_6 in concentrations greater than those calculated from the thermodynamic equilibrium constant at the temperature of the irradiations.

Plutonium hexafluoride decomposes by alpha radiation to PuF_4 and fluorine. A kinetic study of the decomposition of PuF_6 by alpha radiation is being made at ANL.[13] The results indicate that the decomposition rate of gaseous PuF_6 caused by alpha radiation is not a linear function with time. The addition of helium, krypton, and oxygen to PuF_6 decreases slightly the decomposition rate. The addition of fluorine, however, markedly lowers the decomposition rate owing to the recombination of fluorine and PuF_4. The presence of nitrogen increases the PuF_6 decomposition rate through the formation of NF_3. The decomposition of PuF_6 appears to be a surface-dependent reaction. Preliminary data indicate that the rate of decomposition increases with an increase in surface area.

Steindler and Gunther[21,22] have determined the absorption spectrum of gaseous PuF_6 from 2000 to 26,000 A and have calculated the molar absorbancy indices. The location and molar absorbancy index of the principal peaks of PuF_6 were tabulated in a previous issue of *Reactor Fuel Processing*.[23] In the fluid-bed fluoride-volatility process, a simple nondestructive method of analysis for PuF_6 in mixtures of volatile hexafluorides is required. A method based on the absorption spectra of UF_6 and PuF_6 has been developed for use in the process.[22] It has been established that the spectrum of a one-to-one mixture of PuF_6 and UF_6 is identical with the combined spectra of the individual components, indicating no significant interaction between the gases PuF_6 and UF_6. However, calibration curves must be used for analyzing PuF_6-UF_6 mixtures since deviations from Beer's law have been observed.

A method for analyzing PuF_6 in UF_6 based on the selective reduction of PuF_6 to PuF_4 with SF_4 has been investigated at ANL.[13] The PuF_6 is completely reduced by SF_4, but the UF_6 is not affected. Several mixtures containing 0.5 wt.% PuF_6 in liquid UF_6 were reacted at 85°C with gaseous SF_4 to determine the optimum reaction conditions. An 11-fold stoichiometric excess of SF_4 was sufficient to convert 100 ± 1% of the PuF_6 to PuF_4 in 1 hr. Similar conversion was observed with a 2-fold excess of SF_4, but the time required to achieve complete reaction was 22 hr. A small quantity of uranium was co-deposited with the PuF_4 in the reaction vessel; it was attributed to decontamination of UF_6 by alpha radiation.

Properties of Fluorides

SORPTION OF URANIUM HEXAFLUORIDE

Decontamination of UF_6 produced by fluoride-volatility techniques can be accomplished by an absorption-desorption cycle in a bed of NaF pellets. In the fused-salt volatility process developed at ORNL, UF_6 and other volatile fluorides pass through a bed of NaF at 400°C immediately downstream from the fluorinator; next the UF_6 and certain volatile fluorides are sorbed by NaF at 100°C. Molybdenum hexa-

fluoride is separated from the UF_6 by desorption at about 150°C, and the UF_6, NpF_6, and TcF_6 are desorbed as the temperature of the NaF bed is raised to 400°C. The neptunium and technetium fluorides are then selectively sorbed by MgF_2 at 100°C. Both laboratory-scale and engineering-scale studies are being carried out at ORNL to obtain data useful for the design of sorbent systems. In particular, studies are directed toward improving the capacity, specificity, and stability of NaF and MgF_2 sorbents.[14]

During repeated sorptions and desorptions of UF_6 on NaF pellets, the pellet structure is broken down, and a finely divided low-density powder is produced. The capacity of the NaF pellets to sorb UF_6 is appreciably reduced after the first sorption-desorption cycle but gradually increases in subsequent cycles. The initial sorption of UF_6 by the NaF pellet is dependent on temperature, UF_6 concentration, void fraction, and specific surface area. The temperature dependence of the rate of sorption at a point in the pellet has been shown to be of the Arrhenius type; thus the total sorption capacity for a pellet decreases as the temperature is increased. The dependence of sorption capacity on the concentration of UF_6 is due to different transfer mechanisms for diluted and pure UF_6. For impure UF_6, transfer occurs by diffusion through stagnant diluent gas; for pure UF_6 transfer occurs by forced flow resulting from decreased pressure within the pellet. The sorption capacity for pure UF_6 is about 30% of theoretical and has little dependence on sorption temperature. The dependence of sorption capacity on the void fraction results from the requirement that the sorbed UF_6 must occupy a volume dictated by the density of $UF_6 \cdot 2NaF$ (4.13 g/cm^3 at 26°C). Rate of sorption is initially dependent on the available surface; thereafter it is also affected by the thickness of the surface layer of the complex, which, in turn, is inversely proportional to the specific surface area.

During desorption of UF_6 from the NaF pellet, mechanical damage to the pellet may occur. The extent of damage is a function of the original void volume, temperature of desorption, rate of UF_6 removal, and the temperature to which the NaF is subsequently subjected. In the absence of fluorine, the U(V) complex is formed; it blocks the movement of the UF_6 in the pellet and further reduces the capacity of the NaF for UF_6.

In engineering-scale studies[14] the relations between the life and capacity of NaF pellets and their physical properties were determined by cyclic sorption and desorption of UF_6 on deep beds of pellets. The capacity of the beds for the sorption of UF_6 from a UF_6-N_2 stream was measured under specified conditions of flow rate, temperature, composition, and pellet history by trapping the UF_6 that passed through a bed. It was observed that both pellet life and capacity depended primarily on the void fraction. A high void fraction (0.50 or more) tended to reduce pellet life to less than four sorption-desorption cycles before degradation became severe. Pellets with a low void fraction (0.35 or less) could be recycled more than 20 times. However, pellets that had a low fraction of voids also had a lower sorption capacity for UF_6.

In laboratory-scale studies of UF_6 sorption on NaF,[14,24,24a] the existence of three compounds has been demonstrated, namely, $UF_6 \cdot NaF$, $UF_6 \cdot 2NaF$, and $UF_6 \cdot HF \cdot 2NaF$. Analogous MoF_6 and WF_6 compounds have been prepared and their dissociation pressures measured. The temperature dependence of the dissociation pressures of type $MF_6 \cdot 2NaF$ and $MF_6 \cdot NaF$ compounds is shown in Figs. III-2 and III-3. The equations for the dissociation pressures of the hexafluorides of the $MF_6 \cdot 2NaF$ type compounds are as follows:

For UF_6,

$$\log P_{mm} = 9.25 - \frac{4.18 \times 10^3}{T}$$

For WF_6,

$$\log P_{mm} = 8.80 - \frac{3.99 \times 10^3}{T}$$

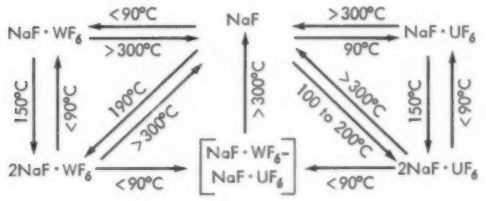
For MoF_6,

$$\log P_{mm} = 8.27 - \frac{2.87 \times 10^3}{T}$$

where P_{mm} is the pressure in millimeters of mercury and T is the temperature in degrees Kelvin.

Compounds that have been prepared by sorption-desorption reactions of NaF with UF_6 and WF_6 are shown in the accompanying diagram.[25] Sorption proceeds rapidly at the lower temperature at 200 mm Hg pressure; desorption proceeds rapidly at the higher temperature

near 1 mm Hg pressure. The apparent compound $NaF \cdot WF_6$-$NaF \cdot UF_6$ does not appear to be a mixture since the sum of the individual dissociation pressures of $NaF \cdot WF_6$ and $NaF \cdot UF_6$ does not equal the dissociation pressure of the compound. The composition of the gas phase over the apparent compound during desorption varies with temperature.



Reactions of UF_6 and WF_6 with lithium, potassium, rubidium, and cesium fluorides have been characterized[14] at temperatures from 100 to 450°C. Lithium fluoride did not react with WF_6 below 435°C. No reaction of LiF with UF_6 occurred until a temperature of 370°C was attained; the product of the reaction was a U(V) compound. When UF_6 and WF_6, respectively, contacted KF, RbF, and CsF separately, compounds with compositions approximating $2UF_6 \cdot 3KF$, $WF_6 \cdot 2KF$, $UF_6 \cdot 1.7RbF$, $WF_6 \cdot 2.1RbF$, $UF_6 \cdot 0.8CsF$, and $WF_6 \cdot CsF$ were formed. These compounds evolved only a small quantity of the metal hexafluorides on heating to 400°C.

REMOVAL OF TELLURIUM HEXAFLUORIDE FROM GAS STREAMS

Radioactive tellurium in effluent gases from fluoride-volatility processing represents a possible source of atmospheric contamination. The tellurium is probably present in the effluent gas stream as the volatile hexafluoride TeF_6 (boiling point, 38°C) although some lower valent, less volatile fluorides might originate through

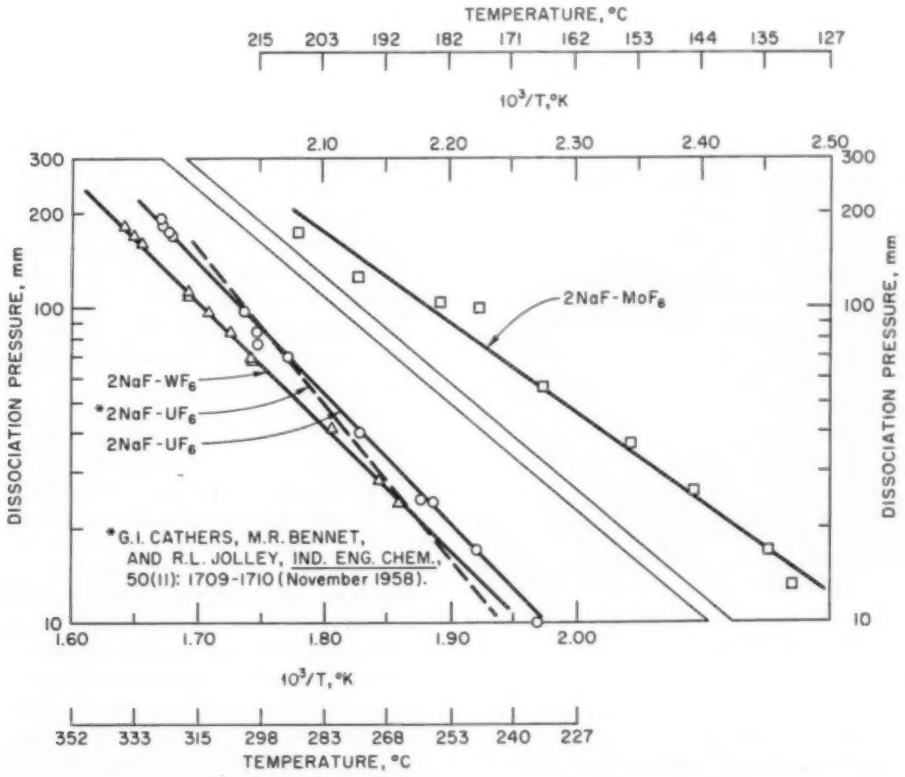


Fig. III-2 Dissociation pressures of $2NaF \cdot MF_6$ compounds.[24a] (Published by permission of Inorganic Chemistry.)

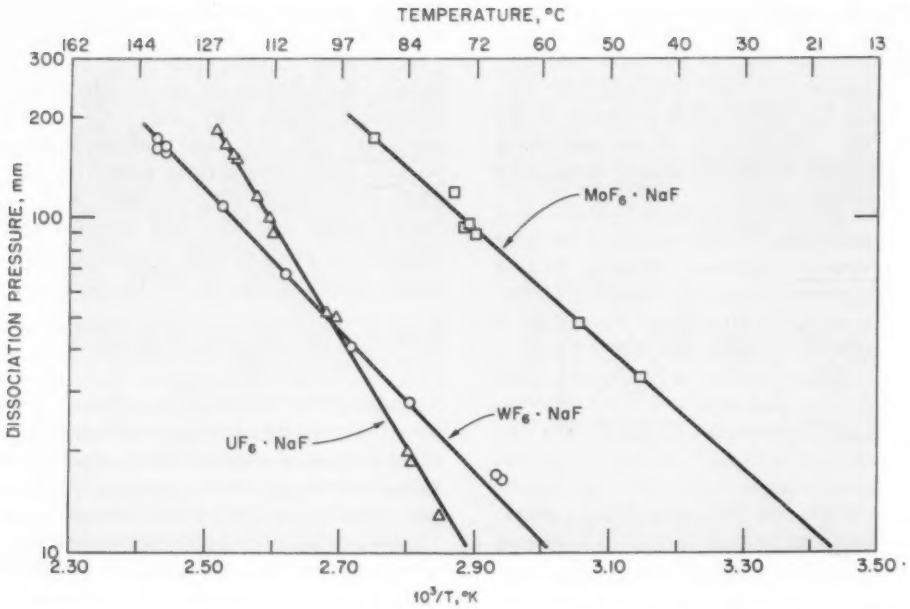


Fig. III-3 Dissociation pressures of $MF_6 \cdot NaF$ compounds.[24]

reduction. A caustic-spray absorption system used in the ORNL fused-salt volatility pilot plant for fluorine disposal has been shown[26] incapable of completely removing tellurium from the effluent gas stream. Laboratory tests[14] have shown that passage of the effluent gas stream through a bed of nickel mesh at 400 to 500°C effectively removes tellurium from the gas. The mechanism for tellurium retention in a hot-nickel bed is probably a combination of chemical reduction and diffusion of elemental tellurium into the nickel.

CHLORINE TRIFLUORIDE

Chlorine trifluoride has been used in several applications as a fluorinating agent for the production of UF_6 from uranium compounds. Vincent and Gillardeau[27] have prepared a monograph on the physical, chemical, and physiological properties of ClF_3.

The reaction of ClF_3 with UO_2F_2 to produce UF_6 is being studied at the Paducah Gaseous Diffusion Plant.[28] Previous work, reported in *Reactor Fuel Processing*,[29] showed that this reaction proceeds according to Eqs. 1 and 2, the stoichiometry approaching Eq. 2 for long reaction times or high temperatures.

$$2ClF_3 + UO_2F_2 \rightarrow ClO_2F + ClF + UF_6 \quad (1)$$

$$4ClF_3 + 3UO_2F_2 \rightarrow 3O_2 + 3UF_6 + 2Cl_2 \quad (2)$$

At 54°C the reaction proceeds according to Eq. 1. The heat of reaction has been measured[28] in a nonisothermal flow calorimeter, and preliminary results indicate that $\Delta H_{54°C}$ is approximately 65 kcal per mole of UO_2F_2.

The reaction of ClF with UO_2F_2 has been shown[28] to proceed at 90 to 133°C according to Eq. 3:

$$4ClF + UO_2F_2 \rightarrow UF_6 + 2Cl_2 + O_2 \quad (3)$$

Chloryl fluoride (ClO_2F) is always found in the reaction products initially, but its concentration decreases with time, the rate of decrease increasing at the higher temperatures.

Nikolaev and Shishkov[30] have investigated the fluorination of uranium sulfate, $U(SO_4)_2$, by ClF_3 at 18 to 300°C and have suggested that the reaction occurs in a stepwise manner:

$$3U(SO_4)_2 + 2ClF_3 \rightarrow 3UO_2SO_4 + 3SO_2F_2 + Cl_2 \quad (4)$$

$$3UO_2SO_4 + 8ClF_3 \rightarrow 3UO_2F_2 + 3SO_2F_2 + 4Cl_2 + 6OF_2 \quad (5)$$

$$3UO_2F_2 + 8ClF_3 \rightarrow 3UF_6 + 4Cl_2 + 6OF_2 \quad (6)$$

The overall reaction is represented by the equation

$$3U(SO_4)_2 + 18ClF_3 \rightarrow 3UF_6 + 6SO_2F_2 + 9Cl_2 + 12OF_2 \quad (7)$$

The formation of UF_6 is apparently the result of fluorination of the UO_2F_2 intermediate.

The results of an extensive investigation of the compatibility of welded structural materials with liquid ClF_3 and perchloryl fluoride (ClO_3F) have been reported by Grigger and Miller.[31] Corrosion rates at 30 and 66°C were measured for stressed and unstressed welded alloys of aluminum, nickel, and stainless steel in ClF_3, ClO_3F, and 25% ClO_3F–75% ClF_3. At 30°C corrosion rates for all specimens were <0.1 mil/year. At 66°C corrosion in ClF_3 and 25% ClO_3F–75% ClF_3 was <0.1 mil/year except for type 410 stainless steel (1 to 2.2 mils/year). In ClO_3F at 66°C corrosion was normally below 0.5 mil/year, but with moisture present corrosion rates up to 8.3 mils/year were observed. (J. Barghusen)

Pyrometallurgical Processes

At the recent third Geneva Conference, Burris described the U. S. efforts on pyrometallurgical processes.[32] An extensive discussion of these processes by Pierce and Burris is contained in *Reactor Technology, Selected Reviews—1964* (Ref. 33). These processes provide rapid recycle of fuel discharged from power reactors to reduce out-of-reactor fuel inventories to as low a level as practicable. This is especially important for fast reactor fuels that have high concentrations of fissionable materials. Pyrometallurgical processes are able to handle short-cooled fuels because radiation-insensitive reagents are employed.

EBR-II Fuel Cycle Facility

An important milestone in the development of pyrometallurgical processes was reached in September when processing of the first discharged EBR-II fuel material was begun in the EBR-II Fuel Cycle Facility.[34] Operation of this facility,* which was constructed adjacent to the EBR-II reactor, will provide the necessary information for economic and engineering evaluations of pyrometallurgical purification procedures and subsequent fuel-refabrication operations. The reclaimed fuel will be returned to the EBR-II reactor, thus completing the fuel cycle. The EBR-II complex will provide the first demonstration of a closed fuel cycle and consequently the first indications of the long-time effects of continued fuel recycle. A report on nuclear criticality control in the EBR-II Fuel Cycle Facility has been issued.[35]

The first discharged fuel material (an enriched uranium-fissium alloy) had a burnup[34] of only 0.1%. Fuel burnups approaching 2% are believed to be attainable ultimately. However, the radiation intensity of the initially discharged fuel, 8.3×10^4 r/hr at 1 ft, is probably fairly close to that of higher burnup material. The core subassembly was disassembled in the Air Cell, and the cladding was removed from the fuel pins in the Argon Cell.[34] The fuel pins were chopped into small pieces (1 to 2 in. long), and these were charged to the melt-refining furnace and processed without incident. The pouring yield from the charge of 9 kg was 92.7% (see poured ingot in Fig. III-4, which shows uranium-fissium metal that has been melt refined, poured into a mold, and dumped from the mold). This yield, which is about the same as yields achieved for unirradiated material, is a very

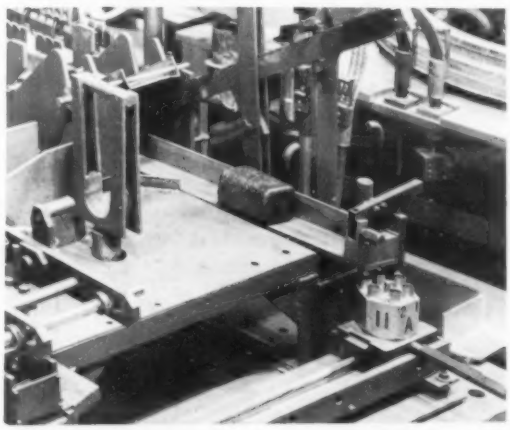


Fig. III-4 Ingot of melt-refined fuel prepared from the first fuel elements discharged from the EBR-II reactor.[34]

*An extensive description of this facility was given in the previous Review.[36]

encouraging result. In the only other work with irradiated material in which runs were performed with only 400-g charges,[37,38] the pouring yields were somewhat lower than those with unirradiated material. Samples obtained by shearing off the protrusions on the base of the ingot (Fig. III-4) are being analyzed to provide information on fission-product removal by the melt-refining process.

The skull remaining in the furnace was successfully oxidized and transferred to a storage container.[34] The oxidized skulls from the melt-refining runs will be stored for some time and ultimately will be processed by another pyrometallurgical process, known as the skull-reclamation process,[39] which is now in a pilot-plant stage of development at ANL.

Halide Slagging

Bennett and coworkers have reported[40,41] on the use of molten halide salts in the melt-refining process to selectively extract rare earths and other highly electropositive fission products from a molten uranium-plutonium-fissium alloy. This process has been distinguished from the present melt-refining process by giving it the name "halide slagging." A report of this work taken from material in an ANL progress report[42] has been published in this Review.[43]

Because of the importance of plutonium in a long-range breeder program, an article on plutonium technology that appeared recently in *Atomics*[44] will be of interest to many readers.

Development of Molten-Metal and Molten-Salt Processes

Several pyrometallurgical processes are based on separations that may be achieved in media solvent in molten metal and molten salt. Separations are achieved by selective precipitation of certain elements and by selective oxidation or reduction reactions and subsequent transfer of the oxidized or reduced species between phases.

EBR-II Skull-Reclamation Process

Complementary to the EBR-II melt-refining processes is the skull-reclamation process[39] that has been developed at ANL for recovery and purification of melt-refining crucible residues (skull material). The second[45] of a series of reports describing development of this process has been issued. This report describes laboratory work that led to the adoption of an oxidation procedure for the removal of melt-refining skulls from melt-refining crucibles. A free-flowing oxide powder that can be poured from the crucible with yields of about 98% is obtained by oxidation with a 20 vol.% oxygen–argon mixture at temperatures of 700 to 800°C. Iodine is the only major fission product to volatilize significantly under these conditions. Plant-scale oxidation equipment has been built, tested, and installed in the EBR-II Fuel Cycle Facility in Idaho.

The remaining steps of the skull-reclamation process are being demonstrated on a pilot-plant scale at ANL. Adequate removals of all fission products except zirconium[46] have been obtained, and efforts are being made to increase zirconium removals. In two recent runs the temperature of operation was lowered from 800 to 700°C. Although fission-product removals were satisfactory (even that of zirconium), a problem of flux foaming was encountered.[46] The problem of foaming is believed to have resulted from incomplete removal of water of hydration of the flux constituents. Methods are being examined whereby the water content of the flux charges can be lowered.

A large 10-in.-diameter by 20-in.-high tungsten crucible, fabricated from 0.18-in. sheet material by welding, has recently been placed in use in the skull-reclamation-process pilot plant.[36] A single tungsten crucible is used for all process steps except the first step (skull oxidation) and the last step (retorting). Weighing about 80 lb, the welded crucible is considerably lighter than pressed-and-sintered tungsten crucibles (500 lb) that have been used previously. The welded crucible has performed well in initial runs.[34]

In the final step of the skull-reclamation process, the solvent metals, magnesium and zinc, are vaporized from the uranium product, an operation known as retorting. Engineering-scale retorting runs that involve 15 kg of zinc and magnesium have been made in isopressed and thixotropically cast beryllia crucibles.[46] These beryllia crucibles have been reused a number of times, but their lives have been limited by the appearance and growth of cracks. Because tungsten crucibles are considered more reliable than beryllia crucibles, consideration

has been given to performing the retorting step in tungsten and then freeing the uranium product, which is frequently stuck to the tungsten, by completely or partially hydriding the uranium.[34] In a preliminary run the hydriding operation was performed without difficulty, and the entire product was easily dumped from the crucible.[34]

An attractive procedure that would eliminate the retorting operation is also under study.[36] This involves hydriding a uranium-metal precipitate contained within a solid shallow layer of a 50 wt.% magnesium–zinc alloy in a tungsten crucible. (In the present process the precipitated uranium and the 50 wt.% magnesium–zinc alloy are dissolved in a 12 wt.% magnesium–zinc solution, and the resulting product solution is then retorted in a beryllia crucible for recovery of the uranium.) Hydriding of the dispersed uranium phase at 320°C caused the alloy layer to break up. The resulting fine powder, containing some larger metallic pieces, was dumped easily from the crucible.[36]

Preparation of Metals by Reduction of Their Compounds

The processes used for the reduction of reactive metals, such as thorium, uranium, and plutonium, are often closely related to steps used in pyrometallurgical processes. Chauvin and coworkers[47] of France have reported on the production of high-purity uranium by electrolysis of molten LiCl-KCl-UCl_3 salt mixtures at 450 to 500°C. Intended principally for fundamental metallurgical studies, high-purity uranium is produced at a rate of about 1000 kg/year. Most metallic impurities are below the limit of detection. The two most important factors in obtaining uranium of high purity are the use of anhydrous salt baths and the thorough removal of adhering salt from the cathode deposit by washing.

Patents have been issued on the following:

1. Fusion electrolysis for the concentration of uranium or plutonium or both in aluminum alloys.[48] The electrolysis is carried out in the presence of a molten salt that contains cryolite. The cathode may be graphite or liquid aluminum. In either case uranium and plutonium concentrate at the cathode, leaving many fission products behind in the original aluminum-alloy phase that serves as the anode.

2. Preparation of alloys of aluminum and actinide metals by suspending oxides of actinide metals (uranium, plutonium, or thorium) in molten chlorides and reducing them into aluminum in the presence of a chlorinating agent as the reaction mass is sparged with an oxygen-containing gas.[49]

3. Preparation of suspensions of thorium oxide in a liquid metal. This patent by Brown and Chitty[50] involves reacting thorium that has been dissolved in a liquid metal with an oxide that is wetted by the metal and is less stable than ThO_2. This is accompanied by violent mixing of the metal phase and sometimes by additional heating to increase the temperature.

Equipment

Eddy-current induction probes for determining liquid levels of molten metals are under development at ANL. The probe consists of dual-wound primary and secondary Nichrome coils wound on a ceramic core. The output of the secondary coil is strongly affected by the presence of a surrounding conductor. The probe is operated in a thermocouple type well and is thought to be readily adaptable to remote operation. Improved performance of probes has resulted from the use of a grooved alumina form that supports and separates the coils and prevents them from shorting out against the well. One such probe has been in service for two months without malfunction or change in characteristics.[46]

Fundamental Studies Relative to Liquid-Metal Process Development

Fundamental information on molten-metal and molten-salt systems is necessary for the logical design of pyrometallurgical processes. A preliminary value for the activity coefficient of plutonium in liquid magnesium of 9.2 ± 0.9 has been reported[46] for the temperature range of 600 to 800°C and a plutonium concentration of 0.08 wt.%. This information will be useful in the design of fuel processes in which magnesium-containing solvents are used.

The diffusivities of uranium in various metal solvents were reported by Hootman, Hesson, and Burris[51] at the 1964 fall meeting of The Electrochemical Society in Washington. The diffusivities of uranium in liquid cadmium, zinc, bismuth, and aluminum, as determined by a capillary-bath technique, are shown in

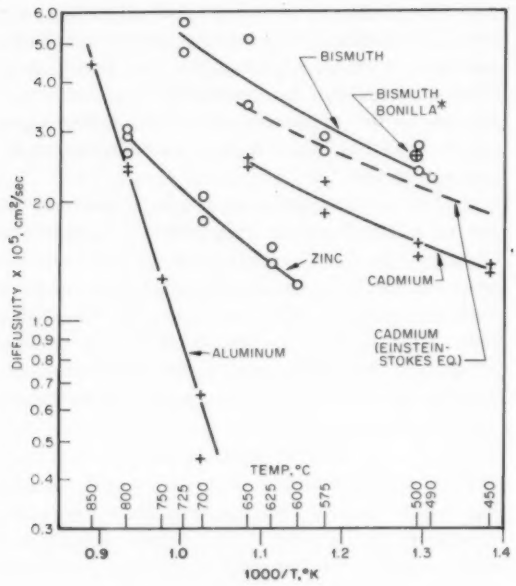


Fig. III-5 Diffusivities of uranium in various solvent metals.[51] The Bonilla point is the value reported by C.F. Bonilla in* Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, *Vol. 9, p. 122.*

Fig. III-5. The diffusivities of uranium in these solvents were somewhat less than those predicted by the Einstein-Stokes equation.

Construction Materials for Liquid-Metal Fuel or Liquid-Metal Process Systems

Alloys of cadmium, magnesium, and zinc are used as solvent-metal media in the liquid-metal processes under development at ANL. Two papers[52,53] on corrosion of various candidate container materials by alloy systems were given at the 1964 fall meeting of The Electrochemical Society. The corrosion of 1020 carbon steel, type 405 stainless steel, and tantalum by the cadmium-zinc-magnesium ternary system at temperatures between 500 and 850°C was reported by Kyle, Nelson, and Burris.[52] Carbon steel (1020) and type 405 stainless steel exhibited excellent corrosion resistance to cadmium-magnesium alloys at temperatures up tc 750°C. Corrosion rates of these materials increased with increasing concentrations of zinc in the ternary alloy. The corrosion of type 405 stainless steel by the cadmium-magnesium-zinc system is illustrated in Fig. III-6. Tantalum exhibited good corrosion resistance to all ternary systems at temperatures up to 850°C, except for those systems with zinc concentrations above 95%.

Nelson et al.[53] reported on the corrosion resistance of tantalum, molybdenum, tungsten, and some alloys of these metals to zinc and zinc-rich alloys, both in the presence and in the absence of molten chloride salts. Tungsten and the alloy molybdenum–30 wt.% tungsten were attacked to a depth, respectively, of less than 1 mil and 4 to 7 mils by zinc and a molten chloride salt in 400 hr at 800°C. Under similar conditions tantalum and molybdenum were severely attacked. It was concluded that only tungsten and certain tungsten alloys are suitable for the containment of zinc-rich alloy and halide-salt systems.

The mechanisms of liquid-metal corrosion and the results of compatibility tests of alkali metals with various metals were discussed in 23 papers presented at a NASA-AEC Liquid-Metals Corrosion Meeting held in Cleveland, October 1963. The proceedings of this meeting have been published.[54] Attention is also directed to three additional issues of *High-Temperature Liquid-Metal Technology Review* which have been published.[55] These reviews are published bimonthly by BNL and contain principally brief discussions of reports published on engineering properties of alkali metals and corrosion phenomena of alkali metals and mercury. (L. Burris, Jr.)

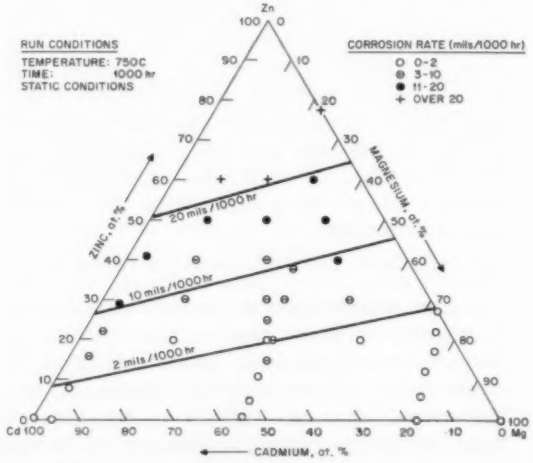


Fig. III-6 Corrosion of type 405 stainless steel by the cadmium-magnesium-zinc system.[52]

Other Nonaqueous Processes

High-temperature processes that use dry-chemical reactions are being developed for the recovery of fissile and fertile material from irradiated oxide and carbide fuels. Gases and molten salts are generally used as reagents and process media. Since these materials are resistant to radiation damage, processes of this type are particularly suited to closed-cycle low-decontamination processing of short-cooled high-burnup fuels. Pyrochemical processes were reviewed briefly at a Brussels conference in 1963 on aqueous fuel processing[56] and at the 1964 Geneva Conference.[32]

Oxide Fuel Processing

Two pyrochemical processes for oxide fuels that are under development in the United States are the salt-cycle process at Hanford Laboratories and the AIROX process at Atomics International.

Salt-Cycle Process

The salt-cycle process is a closed-cycle scheme for processing fuel associated with plutonium recycle.[57–61] The fuel is UO_2 containing a small concentration of PuO_2. The basic steps[61] of the process are summarized in Fig. III-7. The irradiated UO_2-PuO_2 fuel is first removed from its Zircaloy cladding, the UO_2 is oxidized to U_3O_8, and the mixed oxide is dissolved in a molten-chloride bath by sparging the system with chlorine and hydrogen chloride. Uranium is separated from the plutonium by a selective electrodeposition of UO_2 while the melt is being sparged with hydrogen chloride. Additional fuel is then dissolved, and a UO_2-PuO_2 mixture is electrodeposited on a graphite cathode while the melt is being sparged with an oxygen-chlorine gas mixture. The mixed-oxide deposit is stripped from the graphite cathode, crushed, washed with water, re-

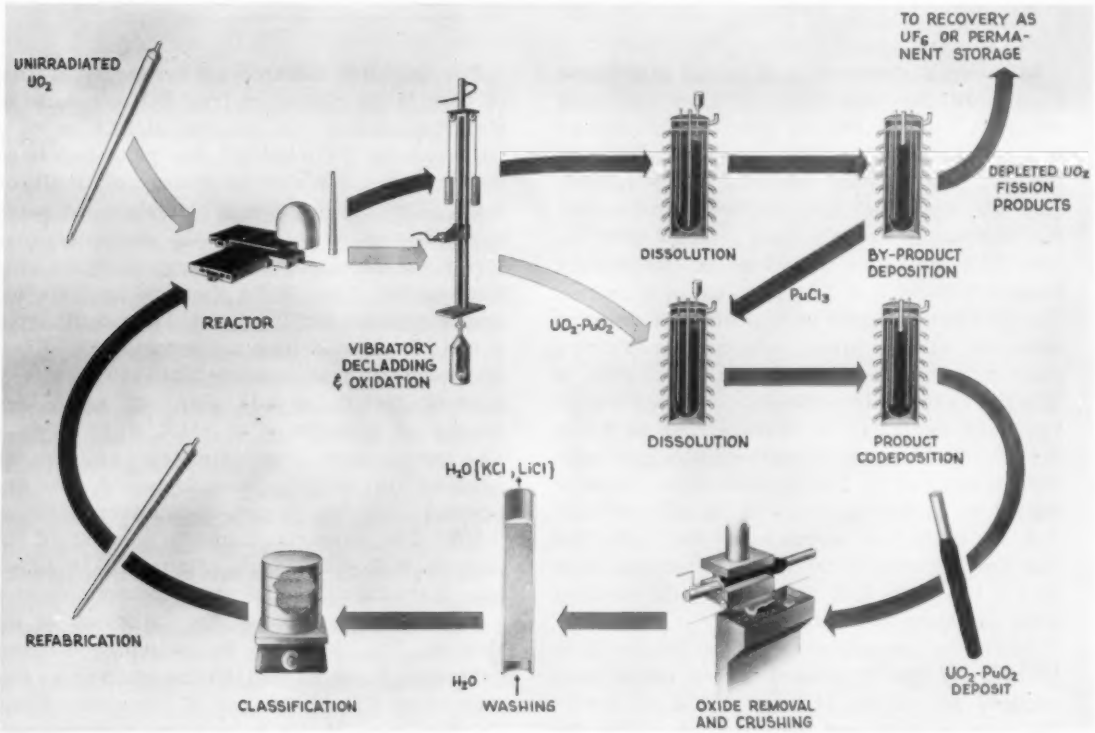


Fig. III-7 Close-coupled plutonium recycle system[61] (Hanford salt-cycle process).

duced with hydrogen if necessary to form stoichiometric UO_2, and classified into the proper size fractions for the fabrication of new fuel by vibratory compaction. The process[60] can be varied, as shown in Fig. III-8, to produce either (1) essentially uranium-free PuO_2 via chemical precipitation of PuO_2 by sparging the melt with an oxygen-chlorine mixture or (2) a UO_2-PuO_2 solid solution by electrolytic co-deposition.

dissolutions were performed in a 20-liter fused-silica pot. The oxide was charged to the molten LiCl-KCl bath in the dissolver; then dried premixed HCl-Cl_2 gas was sparged through the system. An annular submerged gas lift proved effective in efficiently contacting the gas with the oxide so as to achieve rapid dissolution rates. The principal fission products volatilized during the dissolutions were ruthenium, zirconium, and antimony.

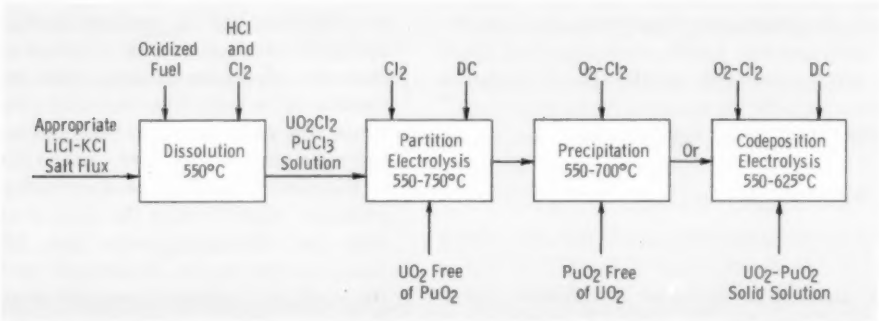


Fig. III-8 Summary flow sheet[60] of the Hanford salt-cycle process.

An overall description of initial pilot-plant studies of the salt-cycle process has been reported.[61] These studies have been conducted with irradiated fuel in a high-level radiochemical facility. The starting material was Zircaloy-clad UO_2-PuO_2 fuel that had been irradiated in the Plutonium Recycle Test Reactor (PRTR). The clad fuel rods were bisected to produce half-rods about 4 ft long by $\frac{1}{2}$ in. in diameter. The fuel was removed by vibrating the inverted half-rods with an air-driven hammer. Thirty-eight half-rods that contained 0.5 wt.% PuO_2 in UO_2 and had been irradiated to 300 Mwd/metric ton were declad in an average time of 5 min per half-rod. Ten additional cold-swaged half-rods irradiated to 2000 Mwd/metric ton were declad in an average time of 30 min per half-rod. In tests with unirradiated fuel rods that had been fabricated by various methods, less than 0.1% of the fuel remained in the cladding after vibratory decladding.

After the decladding process, 10- to 25-lb batches of the irradiated mixed oxide were exposed to air for 24 hr at 450°C to convert the UO_2 to U_3O_8 and thereby to decrease the particle size of the oxide to improve its dissolution rate in a LiCl-KCl salt bath. The

The partition electrolysis for the separation of essentially plutonium-free UO_2 consisted of electrodeposition and the use of HCl or HCl-Cl_2 sparging to maintain the plutonium in an unoxygenated low-valence state, i.e., $PuCl_3$ or $PuCl_4$. The distribution of plutonium and rare-earth fission products in the deposited material was determined by sampling cross sections of the deposits for chemical analysis and then autoradiographing them. The results from a typical cross section are shown in Fig. III-9. This deposit was produced at 550°C with a current density of 0.12 amp/cm^2 and a gas sparge of 3 liters of 30 vol.% HCl–70 vol.% Cl_2 per minute. Approximately 26% of the uranium in solution was deposited, and the product had an oxygen-to-uranium ratio of 2.002. The average plutonium content of the deposit was 0.006 wt.%. Figure III-10 shows the instantaneous plutonium decontamination factor as a function of the thickness of the deposit. The plutonium decontamination factor increased from an initial value of 35 to a value exceeding 250 by the end of the electrolysis. In other runs it has been shown that over 99% of the uranium can be deposited with a final instantaneous plutonium decontamination factor

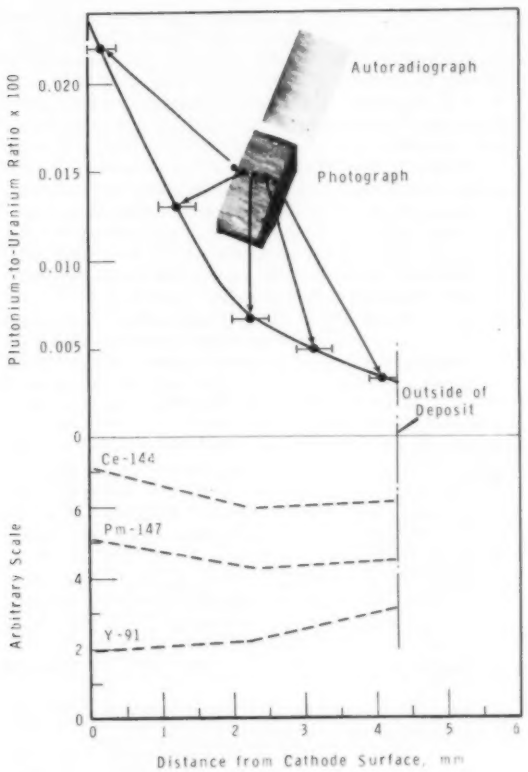


Fig. III-9 Distribution of plutonium and rare earths across a deposit during partition: Run H-6 (Ref. 61).

in excess of 100. During the partition electrolysis the rare-earth fission products tended to remain in solution with the plutonium, but their behavior differed somewhat in that their concentrations did not vary significantly with the depth of the UO_2 deposit.

For the codeposition of uranium and plutonium dioxides, an oxygen-chlorine mixture was employed as the sparge gas. The oxygen served to convert the plutonium to plutonyl(VI) ion, which was reduced electrolytically to form PuO_2. The presence of chlorine was necessary to prevent chemical precipitation of PuO_2. Careful control of the conditions was required during the codeposition procedure to maintain a uniform plutonium-to-uranium ratio in the deposit. Figure III-11 shows a cross section of a typical product. This deposit was obtained at 550°C with a current density of 0.12 amp/cm^2 and a gas sparge of 2 liters of 90 vol.% O_2–10 vol.% Cl_2 per minute. The oxygen-to-uranium ratio of the product was 2.012, and the overall plutonium enrichment factor was 0.94. In this experiment the rare-earth fission products showed a concentration gradient in the deposit which suggests that separation of rare earths may be improved. For adequate removal of neutron poisons, it would be desirable to increase the rare-earth decontamination factor from the value of about 3, obtained in this run, to a value of approximately 6.

The use of graphite cathodes coated with less than 0.5 mil of pyrolytic graphite made it possible to strip the oxide deposits mechanically with less than 20 ppm carbon in the product. The mixed oxide was crushed, washed, and sized to yield a product suitable for refabrication by vibratory compaction.

In the development work on the salt-cycle process, two methods of instrumental analysis are of particular interest. Further work was reported on the direct determination of fuel burnup by beta-gamma anticoincidence counting of ^{137}Cs in mixed fission products.[58] Among the various scintillators tested for beta counting, a gel scintillator proved very promising. If all gammas that are coincident with a beta are rejected, a gamma spectrometer can be

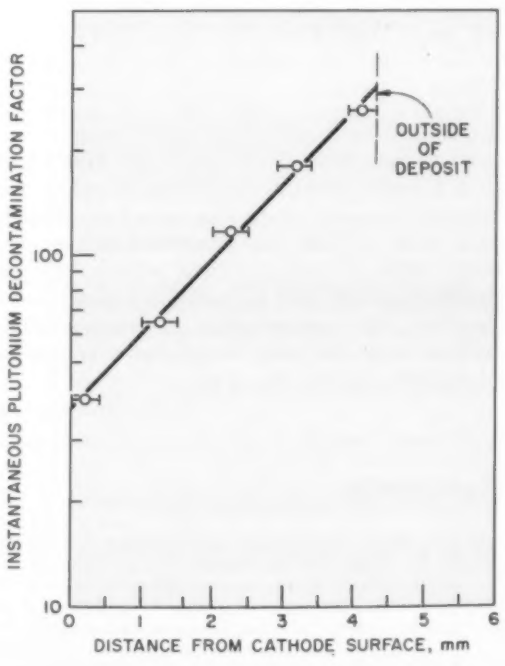


Fig. III-10 Plutonium decontamination factor during partition electrodeposition of UO_2: Run H-6 (Ref. 61).

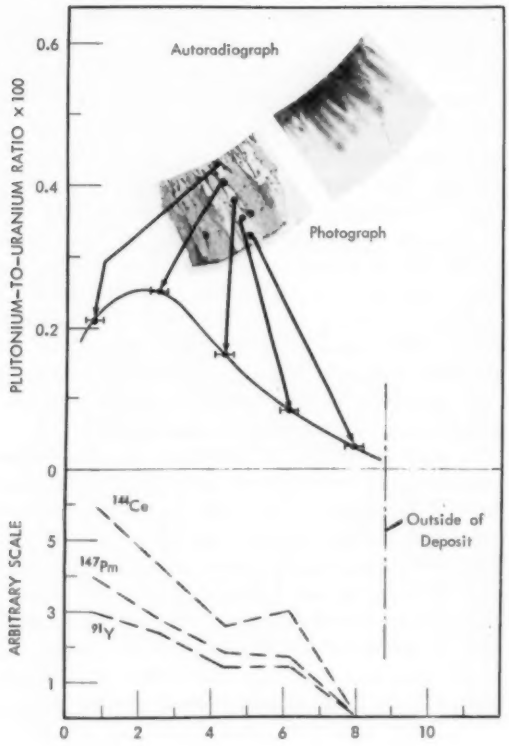


Fig. III-11 Distribution of plutonium and rare earths across a deposit during codeposition: Run H-2 (Ref. 61).

used to determine ^{137}Cs within less than ±1.5% in a 1.5-year-old fission-product mixture. The other instrumental technique uses a quartz light pipe with a $\frac{1}{2}$-in. gap immersed in a molten salt.[59] With a tungsten light source, an appropriate filter, and a cadmium sulfide photodetector, the concentration of uranium(IV) in molten salts has been measured over a concentration range of 0 to 2 wt.%.

(R. K. Steunenberg)

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Section

IV

Reactor Fuel Processing

Waste Disposal

Management of Tritium in Fuel-Processing Wastes

A general review[1] of the tritium waste problem has been made at Oak Ridge National Laboratory (ORNL). The following discussion is taken from this review.

Tritium, 12.3-year ^{3}H, is produced in the fission of ^{235}U, with a yield of about 0.01%, and it merits special consideration from the standpoint of its management in wastes from fuel processing because it is unresponsive to separation and concentration by conventional procedures for treating waste. In fuel processing about 25% of the tritium appears in the dissolver off-gas and is released through the stack. Nearly all the remainder appears as tritiated water in the evaporator condensates and is safely released to the ground water at the sites of existing United States processing plants.

The extent to which present practices can be applied to the future management of tritium-bearing wastes from recovery of power reactor fuels is unclear. Based on recent predictions of nuclear power growth in the U. S., the annual production of tritium may be expected to rise from about 15,000 curies in 1968 to about 6 million in the year 2000. The accumulated production, allowing for natural decay, should rise from 15,000 curies to about 30 million in 2000.

If this tritium could be uniformly dispersed throughout the environment, the resulting increase in background would be of little significance. In the actual case, however, a fuel processing plant will have only its immediate environs available for dispersion, and the capacity of those environs will depend on the rate that tritium is released as well as on the many environmental factors that pertain to that particular site. The rate of tritium release will be determined by the irradiation history of the fuel and its rate of processing by the plant. While the earliest plants may be sized, because of low processing requirements, to handle only a ton or so of fuel a day, there will be a strong economic incentive to increase the capacities of individual plants as the nuclear power industry grows and to situate them less remotely.

Three possibilities other than those in current use at U. S. production sites for the disposal of tritium-bearing wastes are: (1) dilution and release directly to surface waters; (2) distillation into the plant off-gas system and release up the stack; and (3) recycle of evaporator tritium to build up in the concentrated high-level waste stream, which is subsequently stored for decay. It is probable that none will offer the best answer for all future situations but that all three may eventually be utilized to the fullest practical extent.

The quantity of tritium that can be released to surface waters can be computed within the limitations that (1) the concentration shall not exceed $1/10$ the maximum permissible concentration in water (MPC_w) for continuous occupational exposure, or 3×10^{-3} $\mu c/cm^3$, at the boundary of the controlled zone, and (2) the concentration shall subsequently not exceed the ICRP-recommended level for the general population of $1/30$ the MPC_w, or 1×10^{-3} $\mu c/cm^3$. If the controlled zone borders a stream of any significant size, the first of these restrictions is controlling.

A ton of fuel irradiated to 16,000 Mwd at a specific power of 16 Mw contains about 200 curies of tritium, which would require about 18 million gallons of dilution capacity for it to be released from the controlled zone at $1/10$ the MPC. The total aqueous effluent from a plant operating with a Purex process flowsheet may be as much as 10^6 gal per ton of fuel processed, but this is far short of the requirements for tritium dilution. The most practical means of achieving the on-site dilution requirement would be to have available for this purpose a creek or small river flowing through the controlled area. To meet the specification for use by the general population, this stream would have to flow into a larger body of water to achieve additional dilution by a factor of 3 or more .... It is concluded, therefore, that with restrictions as presently interpreted, the alternative of release to surface waters is of very limited applicability as a general case.

Distillation into the plant off-gas may provide an acceptable means of releasing tritium and other fission product contaminants in the evaporator condensates. It is estimated that about 1200 curies of tritium per day could be released from a 100-m-high stack under very unfavorable atmospheric conditions (mean windspeed of 3 mph and extremely unstable conditions) without exceeding $1/10$ the maximum permissible concentration in air (MPC_a) for continuous occupational exposure of 2×10^{-7} curies/cm^3 at any point near the ground. This allowable rate of release would permit a continuous fuel-processing rate equivalent to 96,000 Mw (thermal),

which is the predicted size of the nuclear power economy in about 1985. A single plant of this capacity may not be in existence until an even later date . . . . While it is believed that atmospheric concentration is probably the more important factor in determining allowable tritium releases, additional work will be required to establish ground tolerances and the mechanisms for estimating deposition rates following stack releases under different climatic conditions . . . .

While a total recycle of aqueous streams is technically possible, in practice it might be a rather complex and expensive proposition. The tritium concentrations in such streams would be expected to build up to about 30 times their original values. In this proposed situation, other fission products, especially ruthenium, would also build up in various streams. Presently uncontaminated process makeup areas would become radiation zones requiring safety precautions and limited personnel access.

Possibly the most important aspect in determining the feasibility of recycling condensates, which average in volume about 10,000 gal per ton of fuel processed, would be the demonstration of how effectively the organic content of these streams could be controlled. The so-called organic "cruds," composed principally of butyl phosphates and hydrocarbons, are steam-stripped during evaporation and would require removal from the condensates before recycling if operating difficulties were to be avoided. Suitable techniques have not as yet been demonstrated.

Treatment of Liquid Wastes by Ion Exchange

Development work has continued at ORNL on the scavenging-precipitation ion-exchange process, which decontaminates the large volumes of slightly contaminated water wastes that result from nuclear fuel processing.[1,2] The decontamination is achieved in two steps: (1) a scavenging-precipitation treatment that serves as a head-end step for the removal of a portion of the activity and the reduction of hardness-ion (calcium and magnesium) content, followed by clarification and filtration of the treated process waste; and (2) an ion-exchange step for sorption of the cesium and strontium remaining. Three modifications[1] to improve this process have been evaluated in laboratory-scale and pilot-plant tests with ORNL low-level-activity waste (LAW) solution. They are (see Fig. IV-1): (1) the use of an activated alumina column to remove phosphates, whose presence hinders hardness-ion removal from untreated raw waste; (2) the recycle of the acid regenerant waste from the cation exchanger together with grundite clay to the main stream entering the flash mixer in order to eliminate the separate processing of the acid regenerant; and (3) the use of anion exchange for additional removal of ruthenium and cobalt remaining in the waste after treatment in the cation exchanger.

Laboratory-scale tests of the modified flow sheet demonstrated that a fluidized chromatographic-grade alumina column removed up to 50% or more of the phosphate (up to 3 ppm) present in 15,000 column volumes of untreated LAW. Subsequent precipitation of the hardness ions in the effluent from the alumina column was considered to be entirely satisfactory. The addition of grundite clay resulted in more than 80% of the cesium processed being found in the settled sludge; without clay, less than 10% was precipitated. Slight improvement in the removal of cobalt and ruthenium was noted. In the precipitation step the decontamination factors for cesium, strontium, cobalt, and ruthenium were 7, 5, 3, and 3, respectively. The average overall decontamination factors (across the sludge clarifier unit and cation exchanger) for cesium, strontium, cobalt, and ruthenium were 630, 6000, 3, and 3, respectively. Strong-base anion-exchange resins Illco TAD-1 and Dowex 21K were tested for removal of ruthenium and cobalt remaining in the effluent stream from the cation exchanger. Both resins showed relatively poor selectivity for ruthenium and no apparent selectivity for cobalt.

For the pilot-plant tests of the modified scavenging-precipitation ion-exchange process, equipment changes were made which included the use of (1) a fluidized bed of activated alumina (Alcoa F-20, 80 to 200 mesh); (2) a 4-ft-diameter agitated clarifier[3] (to replace an unagitated one) having a processing rate of 47 gal/(hr)(sq ft); and (3) recycle of the cation-exchanger regenerant solution. The modified process was demonstrated in three runs. However, in only one of the runs was effluent from the cation resin column further treated in an anion-exchange (TAD-1) column. The concentration of phosphate in 500,000 gal of LAW was reduced from about 2 to <1 ppm, a satisfactorily low level, by passage through the alumina column. The efficiency for phosphate removal was more than 50% for the first 325,000 gal of waste treated (10,000 alumina column volumes). The hardness-ion concentration was reduced from about 70 ppm (as $CaCO_3$) present in the untreated LAW to 7 ppm (as $CaCO_3$) in the clarifier effluent and to 4 ppm (as $CaCO_3$)

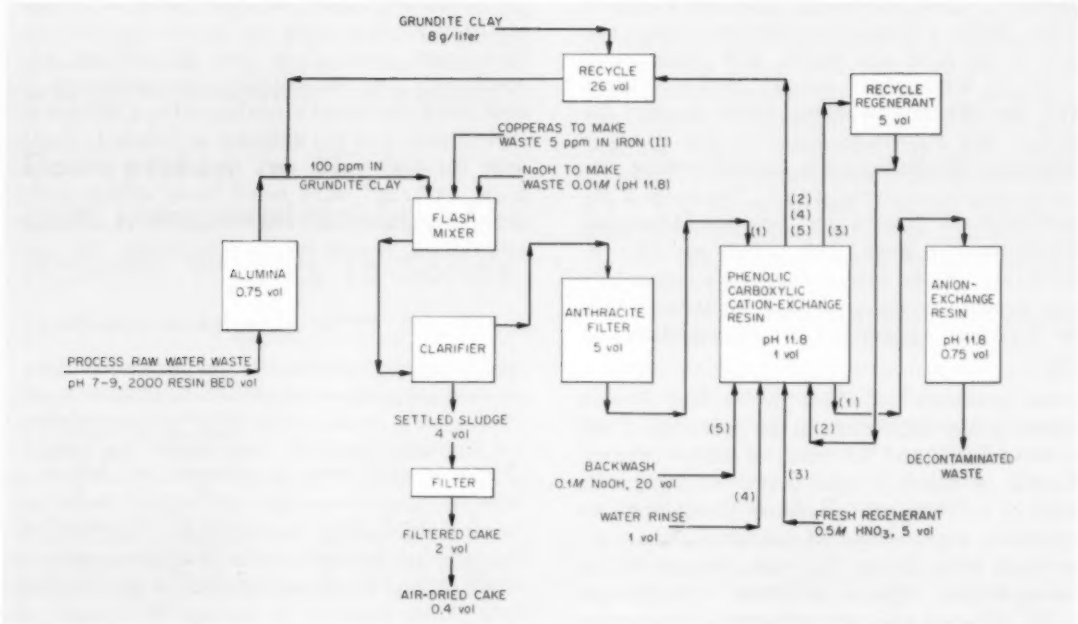

Fig. IV-1 Flow sheet used in tests of the modified scavenging-precipitation ion-exchange[1] process.

in the filtered effluent. The reduction in phosphate concentration is believed to have contributed to the efficient precipitation of hardness ions. Recycling the cation-resin-column regenerant solution and adding grundite clay before the flash-mixing step increased cesium retained in the sludge from 29 to over 60%. The addition of grundite may have possibly reduced strontium retained in the sludge from 80 to 72%. The average overall decontamination factors in the three runs were 1200, 1400, 2.6, and 500 for cesium, strontium, ruthenium, and rare earths, respectively. When the effluent (300 bed volumes) from the cation exchanger was further treated by anion exchange, the overall decontamination factors for ruthenium and cobalt were increased to about 14 and 11, respectively. For fuel-processing plants that require ruthenium decontamination factors greater than about 2.5, the extra cost of an anion-exchange system would be justified. However, it was concluded that the modified process without the anion-exchange system should be satisfactory for treating wastes that are similar to ORNL LAW since the concentrations of all radionuclides of interest in the treated effluents were less than 2% of the MPC_w.

Decontamination of Purex-Plant Wastes at Hanford

At Hanford a pilot plant for the ion-exchange treatment of Purex tank-farm alkaline condensate has been placed in operation.[4–6] The treatment of the condensate is carried out in three steps: (1) a steam-stripping step in which the bulk (>97%) of the ammonium ion and organic material is removed; (2) a filtration and cesium removal step in which the bottoms from the stripping tower, after being cooled, are passed through a precoat filter containing a cesium-selective adsorbent; and (3) an ion-exchange adsorption step in which the filter effluent is first passed through a strong-base anion bed for removal of ruthenium (along with nitrate and nitrite ions) and is then acidified to *p*H 4 before it enters the cation exchanger for removal of strontium, cerium, zirconium, residual cesium, and other radioactive cations. Three runs were made in which a total of 7400 gal of actual plant-level-activity condensate was treated.[5] The steam-stripped condensate was passed (1 gal/min) first through a thin precoat filter bed ($\frac{1}{2}$ in. thick, 0.3 gal) of clinoptilolite and then successively through two ion-exchange columns (6 ft long by 6 in. in

diameter). Each exchanger contained 5.2 gal of resin: Dowex 1 anion resin (hydroxyl form) was used in the first and Dowex 50W cation resin (hydrogen form) in the second. In the filtration step the average decontamination factors for cesium and strontium were < 2. The average ruthenium decontamination factor across the anion-exchange column was 5. The overall decontamination factors for cesium, strontium, and ruthenium were >250, >500, and 23, respectively. In the effluent from the cation column, none of the radionuclides studied exceeded its maximum permissible concentration for water.

The presence of solids in the feed stream causes some difficulties in the operation of the thin-bed filter and the anion-exchange column. Buildup of solids in both pieces of equipment resulted in excessive pressure drops and necessitated replacement of the filter and anion-exchange beds during the runs. Neither 60- to 100-mesh nor 100- to 200-mesh clinoptilolite in the thin-bed filter was effective in removing all the solids. Solids passing through the thin-bed filter appeared to form an agglomerate with the resin in the top portion of the anion exchanger. The chemical composition and behavior of the solids in the alkaline condensate suggest that the solids are primarily organic and contain a high concentration of bacteria. The sources of the solids and the bacteria are being determined. A limited study on removal of these solids by filtration techniques is also in progress. In addition, removal of organic material (kerosene and tributyl phosphate) from Purex tank-farm condensate by steam stripping is being investigated.[6]

Ruthenium Removal by Electrodialysis and Electrodeionization

Hanford is evaluating electrodialysis and electrodeionization techniques as possible methods for the removal of ruthenium from intermediate-level-activity wastes.[6–8] Laboratory-scale electrodialysis tests were carried out using a plant nitric acid (0.01*N*) condensate waste for feed material. In these tests electrodialysis was used to denitrate the waste solution prior to passing it through a sorption column of activated carbon. Initial results showed relatively fast and efficient ruthenium removal as a result of electrodialysis (see Table IV-1).[8]

Electrodeionization on a laboratory scale was tested with three-cell and ten-cell units having throughput rates of 50 and 500 ml/min, respectively. The deionization compartments of both units contained a mixture of one volume of Dowex 50W and two volumes of Dowex 1. Tests with the three-cell unit (membrane transfer area, 247 cm^2) were made using either nitric acid condensate or Purex tank-farm alkaline condensate wastes for feed solutions. The unit

Table IV-1 $^{103-106}Ru$ DISTRIBUTION ON ACTIVATED CARBON[8]

$$\left(\text{Distribution Value } K = \frac{\text{Counts/Ml on 15- to 50-Mesh Carbon}}{\text{Counts/Ml in Solution}}\right)$$

Time, hr	Raw condensate 0.01*N* HNO_3, *K*	60% HNO_3 removed by electrodialysis, *K*	94% HNO_3 removed by electrodialysis, *K*
1	51	1.1×10^2	6.2×10^2
4	1.7×10^2	2.1×10^3	2.9×10^3
72	1.4×10^3	1.5×10^4	$>10^5$
300	2.1×10^3	7×10^4	$>2 \times 10^5$

was operated at a current density of 3.3 ma/cm^2 and a linear feed velocity of 2.5 cm/sec through the deionization compartment. In the test with the acid condensate, some 2600 bed volumes were processed, and the ruthenium decontamination factor obtained was in excess of 100. Greater than 90% of the sorbed ruthenium was eluted from the resin bed with 6*N* HNO_3. Discoloration of the resin bed was observed along the first 50% of its length, which suggested that the bulk of the resin-bed loading occurred in this section. In the tests with the alkaline condensate waste, the following ruthenium decontamination factors were obtained: about 50 when the waste solution was only filtered (through Dicalite) and greater than 100 when the waste solution was first steam stripped and then filtered.

Tests with the 10-cell unit were performed using alkaline condensate waste for feed. The unit was operated for six days, during which 1620 column volumes of waste were treated. The feed flow rate gradually decreased from 500 to 105 ml/min due to the pressure drop caused by the presence of organic matter in the feed. The ruthenium decontamination factor decreased rapidly from 50 to about 15, at which value it remained thereafter. The effectiveness of the electrodeionization method for removing ruthenium was demonstrated by deliberately

shutting off the power to the unit during the test. Within 2 min the ruthenium breakthrough increased from 7 to 60%. Further evaluation of the electrodeionization process is planned.

Conversion of High- and Intermediate-Level-Activity Wastes to Solids

Conversion to Glasses

ORNL is continuing the development of calcination processes for converting high-level-activity wastes to glassy solids. Two procedures, the rising level (RL)-potglass and the continuous (CON)-potglass processes, are being examined.[1,9] The RL-potglass process involves (1) feeding a concentrated aqueous plant waste containing glass-forming additives directly into the pot, (2) vaporizing the liquid, and (3) melting the solid residue to a glassy solid. With proper melt formulation the operating temperature of the pot should be 900°C or lower. As the level rises in the pot, three phases (see Fig. IV-2) are present: liquid glass at the bottom, a small solid interface, and a small liquid supernatant pool. The development of this process on a semiengineering scale has been completed.[10] The fixation of simulated high-level-activity wastes [TBP-25 (aluminum), Purex, and Darex (stainless steel)] was successfully demonstrated in experiments using phosphate as the principal fluxing agent in 4-in.-diameter by 24-in.-high stainless-steel pots. Because these experiments were satisfactory with respect to flow rate, product quality, and corrosion rate, larger scale engineering tests are being carried out in 8-in.-diameter by 88-in.-high pots. (The initial results of large-scale engineering tests were reported in a previous issue of *Reactor Fuel Processing*.[9]) During the course of the semiengineering-scale fixation experiments, thermocouples and electrical conductivity probes successfully located the level of solution, calcine, and melt in the pot.[10] The electrical conductivity probes were shown to be potentially useful as control devices in this calcination process. (Allemann and associates[11] at Hanford have reported the successful monitoring of liquid levels by means of radiation monitors during pot calcination of actual plant-level-activity waste solutions.)

In the CON-potglass process, the plant waste containing added glass-forming materials is fed directly into a horizontal melt vessel. The waste is converted directly, i.e., without an intermediate calcination step, to a molten glass that can flow to and solidify in a final storage container. Two principal objectives of this program are: (1) to develop a melter system that uses conventional construction materials and (2) to produce glasses having low melting points and low corrosivity.

In laboratory studies at ORNL,[1] the development of suitable glass formulations for the potglass program is in progress. Since a major objective of the study is to produce glasses that are not very corrosive toward stainless steels, it may be necessary to accept crystalline solids rather than true glasses. This is particularly true of Purex wastes containing

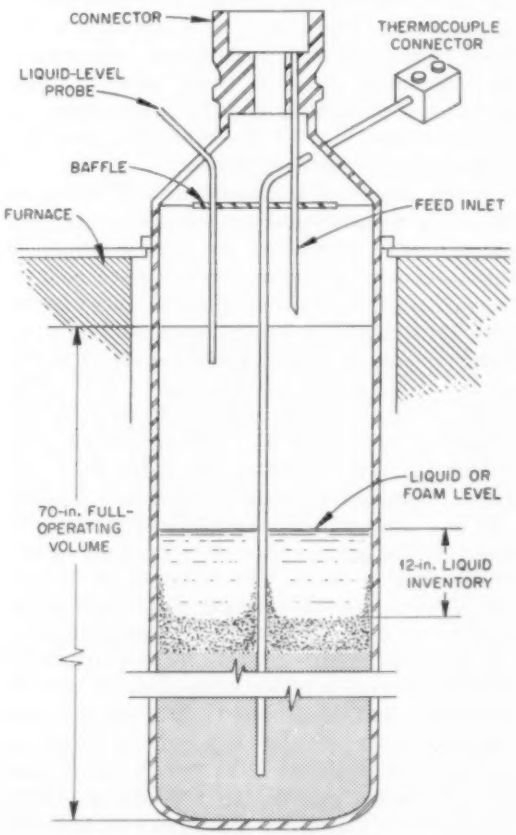

Fig. IV-2 Phase positions in the RL-potglass process.[1]

sulfate. The production of a true glass may not be a reasonable criterion, in any event, since the high temperatures generated by fission-product decay will tend to devitrify most glasses. In general, true glasses are less soluble than crystalline materials of similar composition, probably because of their smaller surface areas for specified shapes and volumes (i.e., smaller roughness factors). The effect of waste oxide concentration in a given glass is not known as yet. However, the marked differences in leach rates for similar compositions of solid products indicate that vitrification is more important than waste oxide content in determining leach rate.

Phosphate was chosen as the primary glass former in the ORNL study for the following reasons: (1) its salts are more easily handled in acid solution than silicates, (2) its salts usually have lower melting points than silicates and have less tendency toward puffiness during meltdown than borates, (3) it appears to be more compatible with sulfate than either silicate or borate, and (4) it is formed by the oxidation of phosphite. The use of phosphite (or hypophosphite) may be desirable for retention of ruthenium in the solid product.

A new series of solid compositions in which lithium was substituted for sodium as a fluxing additive was developed for the fixation of sulfate-containing Purex waste.[1] Since sodium is normally a major constituent of Purex waste (see Table IV-2), the addition of lithium produces a solid with both alkali metals as major constituents. As a general rule, the melts prepared by lithium addition have softening temperatures as low as or lower than the corresponding sodium melts, are more fluid at a given temperature, are somewhat less soluble, and are generally more satisfactory with respect to the operations involved and the nature of the final product. The volatility of sulfate, which is a serious problem with this type of waste, is not increased as a result of substituting lithium for sodium. The volatilization of sulfuric acid is undesirable since the acid is corrosive and constitutes a side stream that requires treatment and disposal. In studies on the fixation of solids from Purex wastes that do not contain sulfate, the addition of PbO to the sodium aluminum phosphate system resulted in the formulation of a number of low-melting (≤700°C) products. Some were true glasses, but their properties (especially corrosion) require further evaluation. A large number of experimental melts were prepared by the addition of lithium, phosphate, aluminum, calcium, magnesium, borate, and/or silicate to simulated waste solutions. Compositions of some satisfactory solid products are presented in Table IV-3.

ORNL is testing the corrosion resistance of construction materials for use in glass-forming systems.[1] In the RL-potglass process, the calcination pot, which also serves as the final storage container, is used only once. Therefore a reasonably high corrosion rate can be tolerated. Penetration up to 150 mils has been selected as a suitable limit for 320-mil-thick single-use pots, although lower rates are desirable.

The suitability of type 304 stainless steel and titanium 45A as construction materials for evaporators used in concentrating Purex-plant wastes was examined. Specimens were exposed to simulated Purex waste solutions (unconcentrated FTW-65 and concentrated 1WW) both with and without glass-forming additives. The results showed that the stainless steel would eventually undergo intergranular attack and

Table IV-2 COMPOSITIONS OF HIGH-LEVEL RADIOACTIVE WASTE[1]

Constituent, gram moles/liter of waste	Purex FTW-65 X3,* 27 gal/ton of U	Future acid† (or reacidified) Purex	Nonsulfate Purex‡
H^+	1.5	0.5	0.5
Na^+	0.9	1.2	0.6
Al^{3+}	0.15	§	0.2
Fe^{3+}	0.30	0.1	0.05
Cr^{3+}	0.06	0.01	0.006
Ni^{2+}	0.03	0.02	0.006
Hg^{2+}	0.0105¶	0.005	§
Ru	0.006	§	§
SO_4^{2-}	0.45	0.2 (0.6)	§
PO_4^{3-}	0.015	§	0.02
SiO_3^{2-}	0.03	§	§
F^-	0.0015	0.0005	§
NO_3^-**	~3.1	~1.6	

*The FTW-65 X3 represents the highest concentration of this waste type that can be conveniently simulated by direct makeup from laboratory reagents without heating.

†Also corresponds to neutralized waste prior to reacidification (i.e., $2Na/SO_4 = 3$); $SO_4 = 0.6$ after reacidification.

‡Estimated from consideration of various Savannah River plant flow-sheet wastes.

§Content not specified.

¶Maximum.

**Enough NO_3^- to balance in each waste.

Table IV-3 COMPOSITIONS OF SOME TYPICAL SOLID PRODUCTS FROM FIXATION OF PUREX WASTES[1]

	FTW-65 waste X3		1WW waste 1WW-1	Nonsulfate Purex
	FTW-1	FTW-3		
Additives, gram moles/liter of waste				
H_3PO_4 or H_3PO_3	1.02	2.27	2.27	0.75–1.5
$Al(NO_3)_3$	0.5	1.0	1.0	
LiOH	1.14	2.53	2.53	
NaOH		1.4	1.4	
$Ca(NO_3)_2$ or $Ca(OH)_2$	0.2			
$Fe(NO_3)_3$		0.16	0.16	
$Pb(NO_3)_2$				0.2–0.3
$Na_2B_4O_7$				
Waste oxides, wt.% (theoretical)	44.5	25.8	32.2	16.9–26.5
Composition, mole % (theoretical)				
Al_2O_3	11.8	11.7	10.4	6.7–9.8
CaO	7.2			
Na_2O	16.3	23.4	18.9	20.1–29.4
Li_2O	20.6	25.7	23.9	
Fe_2O_3	5.4	4.7	6.2	1.7–2.5
Cr_2O_3	1.1	0.6	0.1	0.2–0.6
NiO	1.1	0.6	0.1	0.4–0.6
RuO_2	0.2	0.1	0.04	
SO_3	16.3	9.1	18.9	37.8–54.5
P_2O_5	18.4	23.2	21.5	37.8–54.5
SiO_2	1.1	0.6		
F^-	0.5	0.3		
PbO				14.3–20.1
B_2O_3				
Approx. melting temp., °C	750	825	750	500–700
Approx. pouring temp., °C	900–1000	900	800	600–800
Ratio*	1.22	1.49	1.06	
Percent SO_3 lost (100 min at temperature)	5.3 (900); 0.7†	5.2 (925)	6.2 (900)	
Description	Brown rock; insoluble; noncorrosive at 900°C	Brown rock, insoluble	Hard brown rock; insoluble	Green glass; insoluble

* $\frac{\text{Chemical equivalents } (Na^+ + Li^+ + Ca^{2+})}{\text{Chemical equivalents } (SO_4^{2-} + PO_3^- + BO_3^- + SiO_3^{2-} + F^-)}$.

† Loss in semiengineering test.

that the titanium corroded at a negligible rate. Corrosion rates for the stainless steel varied from 0.1 mil/month in boiling, unconcentrated FTW-65 to 1.4 mils/month in concentrated 1WW. The corrosion rate of titanium was negligible (≤0.04 mil/month) in all cases. Coupling the stainless-steel specimens to titanium had no noticeable effect on the corrosion of the titanium.

Type 304L stainless steel, however, is considered a satisfactory container material for fixation and storage. Successful fixations were carried out in 320-mil-thick pots of this material at maximum operating temperatures of 950 to 1000°C with simulated FTW-65 and TBP-25 waste solutions. In the TBP-25 waste solution, the container was penetrated to about 120 mils after about 120 hr but did not fail.

The conclusions that were drawn from the corrosion data are: (1) corrosion increases rapidly with increase in temperature above about 900°C, but operating temperatures as high as 1000 to 1050°C can be tolerated with stable melts for limited periods of time in containers that will be used only once; (2) the corrosion rate at a given temperature decreases drastically when all the volatile material, particularly water, has been driven off.

BNL Continuous Phosphate Glass Process

Brookhaven National Laboratory (BNL) is continuing the development of a phosphate glass process for incorporating fission products in stable media.[12,13] The entire conversion of the high-level-activity waste is carried out in an all-liquid system, which lends itself to the development of a continuous process whereby liquid media could be transferred from one process step to another. The BNL continuous phosphate glass process is to be demonstrated at Hanford in the High-Level Radiochemistry Facility. Supporting laboratory studies at BNL

have been concerned with the preparation of phosphate glass products from a simulated plant-level-activity Purex waste solution having the following composition (in moles per liter): iron, 0.3; sodium, 1.69; aluminum, 0.177; chromium, 0.017; nitrate, 4.63; and sulfate, 0.44. The phosphate glass products were formed by adding varying amounts of phosphoric acid and iron (Fe^{3+}) to the simulated Purex waste solution. The compositions and descriptions of the resulting melts are shown in Table IV-4. On the basis of physical examination, compositions 1B, 2B, and 3 gave satisfactory glasses, composition 3 being formed readily at 1000°C and compositions 1B and 2B at 1200°C. It is expected that the demonstration experiments at Hanford will initially use glass compositions 2B and 3 (Ref. 13).

Table IV-4 COMPOSITIONS OF PHOSPHATE GLASS PRODUCTS FROM FIXATION OF SIMULATED PUREX WASTE[13]

	Compositions and products				
	1A	1B	2A	2B	3
Quantity of Fe^{3+} added, moles/liter	0.7	0.7	1.2	1.2	
Quantity of PO_4^{3-} added, moles/liter	3.2	4.8	4.8	6.4	3.2
Fe^{3+}, mole %	16.4	13.04	18.27	15.33	5.6
Na^{+}, mole %	27.8	21.99	20.6	17.27	31.4
Al^{3+}, mole %	2.9	2.3	2.4	1.8	3.3
Cr^{3+}, mole %	0.27	0.22	0.24	0.17	0.32
PO_4^{3-}, mole %	52.6	62.46	58.46	65.41	59.44
Temperature, °C	1200	1200	1200	1200	1000
Product (air quenched)	Glass	Glass	Glass	Glass	Glass
Product (oven cooled)	Slag	Glass	Glass and crystalline	Glass	Glass

BNL is testing platinum and platinum alloys for corrosion resistance.[13] The first of a series of corrosion tests has been completed in which samples of platinum, platinum–3½% rhodium, platinum–5% rhodium, platinum–10% rhodium, platinum–5% iridium, and platinum–5% gold were immersed in Purex phosphate glass at 1200°C for 2500 hr. Only platinum (M1 grade, 99.99% pure) showed no signs of corrosion. (All crucibles used in BNL bench-scale and pilot-plant-scale experiments have been fabricated at M1 platinum.)

Hanford Radiant-Spray Calciner–Continuous Powder-Melter Studies

Hanford is continuing the development of radiant-heat spray calcination[14] for the treatment of high-level-activity aqueous wastes from the Purex process.[5,6,15] In this technique the feed solution is sprayed into the top of a heated column that is maintained at about 700°C. The spray droplets are converted to a powder that falls into a heated pot where the calcination process is completed. Either a sinter or melt results, depending upon the composition of the residue. A continuous melter is also being developed[5,6,15] for converting the powder from the spray calciner to a melt or phosphate glass product which is intermittently discharged to a final storage container.

The radiant-spray calciner (18-in.-diameter unit) and the continuous powder melter were successfully operated as a composite unit in semiworks tests with nonradioactive Purex-based and Redox-based waste solutions.[6] In the tests with the Purex-based wastes, the operation of the composite unit was limited by the relatively low operating temperature (1000°C) of the powder melter (type 310 stainless steel). Waste feeds containing an excess of phosphate usually caused a high pressure drop across the calciner filters. In general, the operation of the filters depended upon the ratio of the added orthophosphate equivalents to the metal cation equivalents in the waste. When the ratio was less than 1, filter operation was good. When the ratio was between 1 and 2, the pressure drop across the calciner filters varied from moderately high to excessive. The increased pressure drop across the filters is believed to result from the condensation of metaphosphoric acid on the relatively cool (~300°C) surface of the filters.

Tests with the Redox-based wastes employed feeds containing added borophosphate and borosilicate. The borophosphate-modified feed was

processed continuously for 15½ hr at calcine powder rates that varied from 3 to 7 lb/hr. The spray calciner operated satisfactorily with the wall temperature at 550°C. The continuous powder melter also operated satisfactorily except for some difficulty caused by excessive foaming. Processing of the borosilicate-modified feed resulted in extensive wall deposits in the spray calciner when the wall was maintained at 600°C. The performance of the powder melter (wall temperature of 1000°C) was very good.

Engineering development[5,6,15] of the radiant-spray calciner and of the continuous powder melter is being done to support the Hanford engineering-scale demonstrations of solidification processes.[16] Laboratory work[5,6,8] is also under way to investigate the effect of composition on properties (melting point, phase separation, and solubility) of glasses formed in the following systems: (1) phosphate-modified Purex wastes, (2) BNL type phosphate glasses that contain large quantities of phosphate (~65 mole % P_2O_5), and (3) an ORNL type glass (containing lithium, calcium, and aluminum) which was developed to reduce sulfate volatilization from sulfate-containing Purex wastes.

In-Tank Solidification

As part of its Waste Management Program, Hanford intends to carry out the solidification of intermediate-level-activity plant waste solutions in large underground tanks (Refs. 5, 6, 8, 17, and 18). The proposed method (see Fig. IV-3) involves concentrating these wastes, which have a low heat-generation rate, to a salt cake.[17] The evaporation will be effected by passing heated air (1200°F) through the waste solution. The air will be sparged directly into the waste solution after passage through the annulus of a hollow shroud tube submerged in the solutions. The annular shroud will perform three functions. First, it will provide a means of introducing the heated air into the solutions. Second, it will act as an air-lift circulator to mix the tank contents. Third, it will allow about

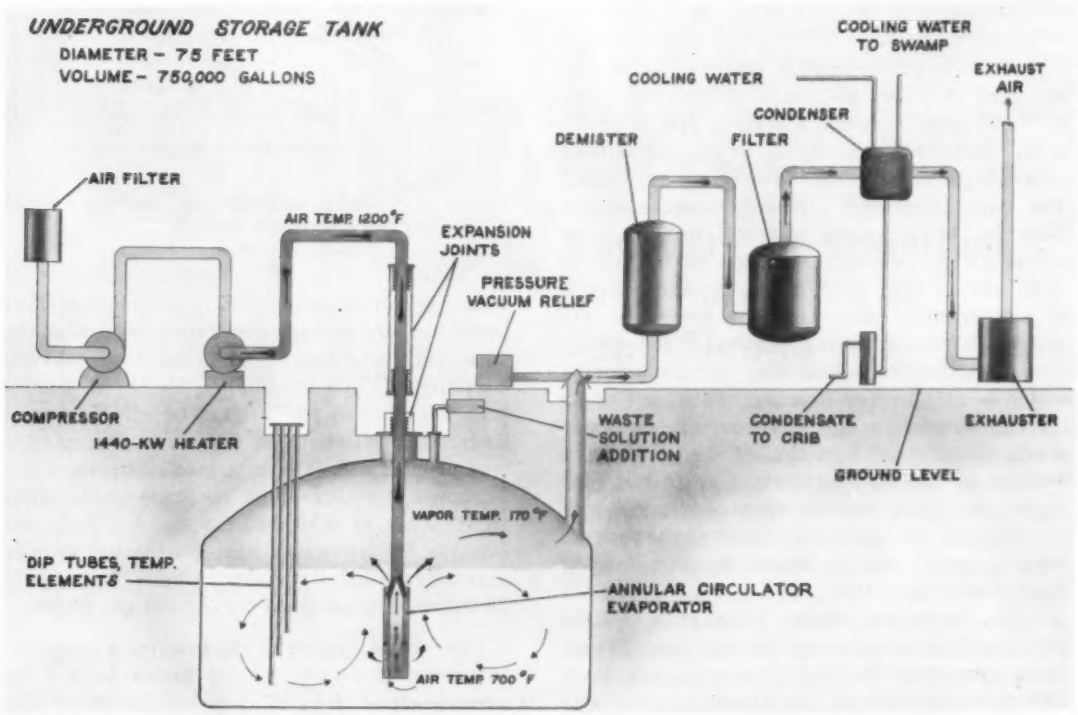

Fig. IV-3 A schematic diagram of the in-tank solidification prototype recently installed in a Hanford intermediate-level-waste storage tank.[17]

one-half of the available heat to transfer to the solution through the shroud-tube walls. The tank effluent gases will be passed through a deentrainer, a filter, and a condenser prior to discharge to the atmosphere. The condensed water will be routed to a crib. Additional wastes will be routed to the tank as the concentration progresses. When the terminal volume and concentration are reached, the tank contents will be allowed to cool and solidify. Only minimal surveillance of the area will be required to assure continued confinement of the radionuclides. Facilities are being installed to concentrate waste solutions to the point of solidification in a 750,000-gal underground storage tank.[6,17] The in-tank solidification equipment is expected to be placed in operation during fiscal year 1965 (Ref. 17).

An alternative method of achieving the necessary concentration of the waste solution is being explored (Refs. 5, 6, 8, and 17). In this concept, sheathed electric heaters, located in the air-lift circulator, are immersed directly in the solution. Although an air-lift circulator is still needed to mix the tank contents, a much smaller quantity of air is used, about 200 scfm in contrast to 4200 scfm in the hot-air system. This improvement is expected to reduce the cost of future in-tank solidification units. Pilot-plant and prototype testing are in progress. Small heaters, up to 10 kw, performed successfully in nonradioactive waste solutions.[6] The only significant difficulty experienced in 2000 hr of operation was the deposition of solids on the unheated section of the heater elements in the vapor space. This deposition of solids might also occur in the heated air concept described above. However, it appears that deposition of solids may be eliminated by suitable design modification or by use of an intermittent water spray. No significant deposition has occurred on the submerged, heated section of the elements. Because of the generally favorable results obtained in the development work, plans are under way to proceed with a plant test of the immersion heating method of evaporation.

Heat dissipation from radioactive wastes solidified in underground storage tanks is also being studied at Hanford.[6,8] A computer study has been undertaken to ascertain the most important factors in the removal of heat from tanks at various rates of heat generation. The tanks are steel-lined concrete, 75 ft in diameter and 32 ft high. They have domed tops and a soil cover of 9 ft. Aqueous radioactive wastes are converted to solid salt cakes up to 16 ft thick by in-tank solidification. The capacity of the tank for heat-generating wastes is determined by the heat-dissipation rate and the allowable maximum temperature.

Preliminary results indicate that the soil thermal conductivity is one of the controlling factors in heat removal.[8] As shown in Fig. IV-4, curves 1 and 2, significantly greater

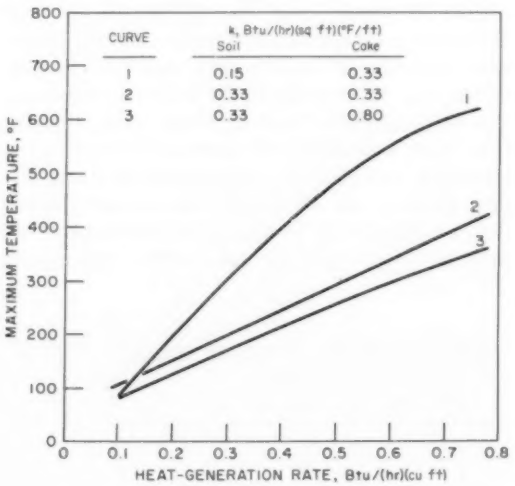

Fig. IV-4 Effect of soil and cake thermal conductivities on maximum temperature.[8]

volumetric heat-generation rates (hence greater concentration of heat-generating wastes in the tank) may be tolerated at a soil thermal conductivity of 0.33 Btu/(hr)(sq ft)(°F/ft) than at 0.15 Btu/(hr)(sq ft)(°F/ft). The effect of cake thermal conductivity in the range examined is less pronounced. A comparison of curves 2 and 3 shows that increasing the cake conductivity from 0.33 to 0.80 Btu/(hr)(sq ft)(°F/ft) increases the allowable heat-generation rate by a relatively small amount. A cake thickness of 16 ft has been assumed for the results shown.

Very little change in the maximum temperature was noted when cake thickness was increased from 4 to 32 ft under the same conditions of heat-generation rate and thermal conductivity of the soil and cake.[6] Also modification of the film coefficients appears to have

little effect on temperature or heat distribution within the system.

Figures IV-5 to IV-7 show the effect of soil thermal conductivity, cake thermal conductivity, and cake thickness on maximum temperature. From these it is seen that cake thermal conductivity is of less importance than soil thermal conductivity. Also, from Fig. IV-5, it can be seen that the concentration of heat-generating wastes may be increased in the storage tank as the soil thermal conductivity increases. Figure IV-7 indicates that above approximately 12 ft in cake thickness there is little change in the maximum temperature of the system for a constant heat-generation rate.

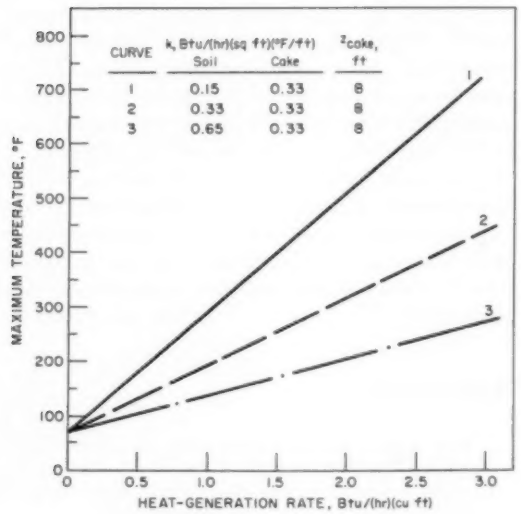

Fig. IV-5 Effect of soil thermal conductivity[6] on heat dissipation from buried radioactive-waste storage tanks.

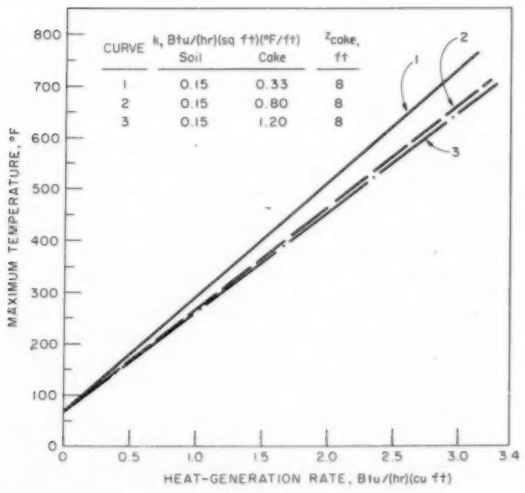

Fig. IV-6 Effect of cake thermal conductivity[6] on heat dissipation from buried radioactive-waste storage tanks.

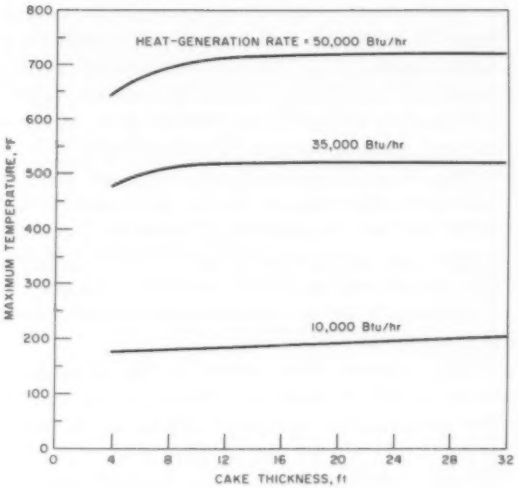

Fig. IV-7 Effect of cake thickness[6] on heat dissipation from buried radioactive-waste storage tanks.

Recovery of Strontium from Purex-Waste Tank Sludge

At Hanford work is being conducted on the removal of fission products from sludge remaining in the Purex-plant waste tanks following the removal of the supernatant solution.[6,19] A lead sulfate carrier precipitation process was developed for removing strontium from acidified Purex sludge waste.[6] In this process the precipitations are carried out at 80°C with feed that is first adjusted to 1 *M* sulfate at *p*H 1. Lead nitrate is added to 0.02 *M* on the first addition and to as little as 0.01 *M* in succeeding additions. After 30 min digestion, the precipitate is allowed to settle, and the supernatant solution is decanted. When the desired amount of precipitate has been accumulated, it

is washed with water or dilute HNO_3 two or three times and metathesized with a mixture of NaOH and Na_2CO_3. The metathesized precipitate is washed with dilute Na_2CO_3 (to remove sulfate ion) and then dissolved in nitric acid. Much of the lead is removed in the metathesis step by adding 15 to 20 moles of hydroxide per mole of lead and digesting at 80°C. The supernatant solutions are separated efficiently from the washed and metathesized precipitates by settling and decanting. This procedure allows the accumulation of several batches of precipitate in the precipitator tank.

The process was tested in the pilot plant using acidified, synthetic Purex sludge waste.[6] The supernatant solutions (15 to 25 in. deep) were decanted at 80°C following a 20- to 60-min settling period. An average loss of less than 5% strontium to the supernatant solutions was found. An overall material balance for the entire process indicated that only 3% of the settled precipitate was lost by decantation.

Other Literature

A review article by Rodger[20] entitled "Safety Problems Associated with the Disposal of Radioactive Waste" has appeared in a recent issue of *Nuclear Safety*, one of the Technical Progress Reviews published by the U. S. Atomic Energy Commission. In this article he reviews the waste problems of the nuclear industry, points out the areas of potential hazard, shows how the hazards are being handled, and discusses some accident situations to indicate the impact they have had on the normal waste-disposal experience.

A safety analysis report[21] on the Waste Calcining Facility[22] at the Idaho Chemical Processing Plant has become available. Details of the safety analysis and extensive information on the process, equipment, and operation procedures are furnished in the report.

A book[23] that describes techniques of handling, treatment, and disposal of low-level-activity wastes has been prepared under the auspices of the Technical Information Division, U. S. Atomic Energy Commission. The book is concerned with practices relating only to continuous operations and not to accidental releases of radioactive materials. Specific examples of U. S. and foreign practices and their results are described.

The International Atomic Energy Agency has issued another report[24] in its Safety Series. This report is the work of an *ad hoc* panel of experts convened by the Agency to study the disposal of radioactive wastes into freshwater. (A previous *ad hoc* panel studied radioactive waste disposal into the sea.[25]) The purpose of the report is to present the principles and practices of radioactive waste management which ensure that the use of freshwater systems will in no way be jeopardized. Major attention has been devoted to disposal in streams, lakes, and subsurface waters. The report also deals extensively with estimation and control of radiation exposure; site and monitoring requirements; and the legal, administrative, and organizational principles of radioactive-waste pollution control at national and international levels. Conclusions and recommendations are presented. (Phillip Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Production of Uranium Dioxide

Reduction of Higher Oxides

The uranium-oxygen system is highly complex. The existence of at least five thermodynamically stable uranium oxides (UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3) has been definitely proved, and several additional oxides have been reported. The system is further complicated by polymorphism, formation of solid solutions, and metastability. Thus the mechanisms governing reduction processes are not readily defined in this system. Vlasov and associates[1,2] have reported the results of a study of the phase transformations in the reduction of uranium oxides. In the reduction of UO_3, U_3O_8, and β-UO_2 (U_4O_9) by acetylene black, the following three schemes have been suggested for the phase transformations that occur during the reduction processes:

For UO_3 reduction

$$UO_{3(\text{amorph})} \rightarrow UO_{2.91} \rightarrow U_3O_8 \rightarrow U_3O_{8-z_{max.}}$$

For U_3O_8 reduction

$$U_3O_8 \rightarrow U_3O_{8-z_{max.}} \rightarrow U_4O_9 \rightarrow UO_{2+x_{max.}} \rightarrow UO_{2+x}$$

For β-UO_2 reduction

$$U_4O_9 \rightarrow UO_{2+x_{max.}} \rightarrow UO_{2+x}$$

In a study of the reduction of U_4O_9 with carbon black and dissociated ammonia,[2] X-ray diffraction analyses of intermediate and end products of the reduction showed that the oxide density gradually decreased as the reduction proceeded to the composition $UO_{2.00}$. On the basis of this observation, it was concluded that the phase UO_{2+x} must have a cubic lattice of the fluorite type with random interstitial excess oxygen and four uranium atoms in the unit cell.

Schiebe and Ermischer[3] have studied the oxidation of UO_2 to U_3O_8 with particular emphasis on defining the intermediate oxide phases formed during oxidation. At relatively low temperatures (160 to 220°C, the actual temperature depending on the reactivity of the oxide powder) a U_3O_7 layer forms on the surface of the UO_2 particles. Complete conversion to U_3O_7 is accomplished by diffusion of oxygen through the layer. Between 280 and 290°C, U_3O_7 is oxidized to a U_5O_{12} phase. Further oxidation proceeds through the formation of an intermediate phase, $UO_{2.6}$ (U_5O_{13}), at 375 to 400°C, and continued exposure to oxygen at this temperature converts the material to U_3O_8.

Sintering Properties of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered UO_2 as the fuel. This fuel must have high density (>93% of the theoretical density) to assure dimensional stability and a high degree of retention of fission gases. Uranium dioxide powders are produced by several different methods, and the sintering properties of the powders are greatly affected by the method of preparation. Considerable attention has been directed toward the development of sintering techniques that would assure a very dense product from all types of UO_2 feed material.

In a study of the sintering behavior of UO_2 bodies, Amato and Colombo[4] have observed that under certain sintering conditions the solarization of sintered UO_2 bodies occurs. Solarization is a decrease in density of sintered bodies to less than the highest value, as a consequence of excessive soaking times at too high a temperature. The final sintered density was

affected by the density of the pressed pellets before sintering. In general, whatever the sintering temperature, the pellets that most rapidly attained high fired density were those which had the highest pressed density. Severe solarization was observed only in cases where organic binders were used in the preparation of the pressed pellets. Solarization was more pronounced at high soaking temperatures and when pellets with high pressed densities were used.

Amato and Colombo[4] attribute solarization of UO_2 bodies to the decomposition of organic binders into gases that accumulate at grain boundaries, thereby forming cavities that tend to inhibit grain growth. For pellets with low pressed densities, the gases evolving from the organic binders have time to escape from the pellets before the sintering progresses sufficiently to close the pores. Thus grain growth occurs, and no solarization takes place. The presence of the binder in pellets with high pressed densities quite rapidly inhibits grain growth, and continued soaking at high temperatures results in enlargement and merging of pores with concomitant decrease in density.

Mansour and White[5] have also observed solarization during sintering of UO_2 powders. They observed that the density of UO_2 pellets, which had been pressed without binder at 66,000 psi and sintered at 1400°C in nitrogen, rapidly reached a maximum of 98% of theoretical, decreased sharply to a minimum (~95% of theoretical), and then slowly increased. They attributed this behavior to the growth of large pores within the compact, followed by elimination of small pores by diffusion of gas from the compact.

Uranium dioxide has a marked tendency to oxidize in oxygen. This behavior is apparent even at room temperature, especially when the UO_2 is in a finely divided state. Workers in France[6] are investigating the conditions under which UO_2 is oxidized in H_2-O_2 gas environments. Oxidation of sintered UO_2 during cooling may be expected to occur if the gas phase is not completely free from oxygen. Distortions of the UO_2 lattice observed in industrial products are similar to those which were produced by exposing UO_2 to an atmosphere containing oxygen at 1×10^{-5} atm pressure.

Several recent publications have been devoted to descriptions of processes and equipment for the production of sintered UO_2 bodies.[7–12] Aparicio, Alonso, and Pedregal[7] at Junta de Energia Nuclear have attempted to characterize the properties of UO_2 powders with respect to sintering qualities. Delmas and Holder,[8] in France, have observed that the quality of sintered UO_2 shapes depends not only on the conditions of reduction from UO_3 but also on processing conditions employed in the conversion of $UO_2(NO_3)_2$ solution to UO_3. In other work, Hauser and Porneuf[9] described a continuous furnace for sintering UO_2 at a rate of 5 tons/month. The characteristic features of the furnace are automatic operation, rigorous control of presintering and sintering atmospheres, and flexibility of temperature regulation so that the thermal cycle can be adjusted to the type of material being sintered. Uranium dioxide pellets are presintered at 800°C in an atmosphere of 10 vol.% hydrogen in nitrogen and then, in a separate section of the furnace, are sintered at 1700°C in an atmosphere of cracked ammonia.

Halle, Brandberg, and Magnusson[10] have described facilities and methods for the production of sintered UO_2 fuel canned in Zircaloy-2 or stainless steel. The report reviews the manufacturing experience at the ASEA Fuel Element Production Plant in Västerås, Sweden, and outlines the various processes used, including powder preparation, pelletizing, canning, and assembly.

A method for densification of UO_2 fuel shapes involving low-temperature sintering in steam has been developed by Brearton.[11] In connection with the process development study, a batch type bottom-loading furnace was designed for processing 125 kg of UO_2 per batch. The furnace was heated by exposed electrical elements made of molybdenum disilicide. Fuel shapes having bulk densities up to 10.8 g/cm^3 were obtained by sintering for 1 hr in steam at 1350°C. The composition of the sintered product was maintained between $UO_{2.010}$ and $UO_{2.003}$ by exposing the sintered oxide at 1100°C for 1 hr to an atmosphere containing 7 vol.% hydrogen in argon.

A process based on isostatic pressing has been described by Bondesan and associates[12] for producing small, sintered UO_2 spheres at high density. The process involves pressing the spheres in a cylindrical die to a density of 6.2 g/cm^3 and sintering the spheres in a hydrogen atmosphere at 1650°C. Uranium dioxide spheres with densities up to 10.65 g/cm^3 have been produced in demonstration tests.

Production of Uranium Tetrafluoride

The standard method for producing metal-grade UF_4 from high-assay uranium concentrates consists of the following steps: (1) dissolving the uranium ore concentrates in HNO_3; (2) extracting the uranium into tributyl phosphate and then into water; (3) converting the aqueous $UO_2(NO_3)_2$ solution to powdered UO_3 by heating; (4) reducing the UO_3 to UO_2 with hydrogen; and (5) treating the UO_2 with anhydrous HF to produce UF_4.

Workers at the National Lead Co. of Ohio (NLCO)[13] have demonstrated the production of UF_4 in pilot-scale equipment by a process (Winlo process) that circumvents the solvent-extraction, denitration, reduction, and hydrofluorination steps of the conventional method. In this process, uranium-bearing residues are digested in a hot HCl-HNO_3 mixture that leaches the uranium and oxidizes any uranium in the 4+ to the 6+ valence state. The uranium solution is prepared for UF_4 precipitation by adding hydrofluoric acid and $CuSO_4$ to the liquor and raising the temperature of the solution to 90°C. Uranium is precipitated as $UF_4 \cdot {}^3/_4H_2O$ by bubbling SO_2 gas into the hot solution. Uranium is reduced from U(VI) to U(IV) by the catalytic action of the cuprous chloride-ion complex ($CuCl_2^-$) that is continuously regenerated from the cupric chloride-ion complex ($CuCl_4^{2-}$) by the addition of SO_2 gas. The $UF_4 \cdot {}^3/_4H_2O$ precipitiate is very dense (3 g/cm^3) and easily filtered. The material is readily dried and then dehydrated at about 370°C, producing uranium tetrafluoride suitable for reduction to metal. A detailed description of the application of the Winlo process to the recovery of uranium from refinery waste streams at NLCO was presented in a previous issue of *Reactor Fuel Processing*.[14]

Cseplo and Fogel[13] have described the pilot-scale equipment used at NLCO in the production of UF_4 by the Winlo process. Because of the highly corrosive nature of the solutions used in the Winlo process, an extensive evaluation was made of construction materials for use in process equipment. Semihard rubber tank linings and Saran-lined piping favorably withstood contact with the Winlo solutions (HF, H_2SO_4, HNO_3, and HCl).

Uranyl nitrate solutions with nitrate concentrations as high as 3.5M could be used as feed for the Winlo process if the nitrate content of the feed solution was reduced to 0.2M or less before precipitation of UF_4. The nitrate ion was decomposed by mixing the $UO_2(NO_3)_2$ solution with HCl and then reacting the resulting solution with formaldehyde in a horizontal-flow glass reactor. Reduction of the nitrate ion before the UF_4 precipitation step is required since the SO_2 gas will preferentially reduce the nitrate ion before reducing the copper catalyst.

Present methods of producing UF_4 in large tonnages involve contacting UO_2 with hydrogen fluoride at elevated temperatures in countercurrent continuous systems. A considerable economic advantage would be realized by operating the process with a small HF excess, preferably with an excess that would allow economic disposal of the off-gases by neutralization. A laboratory study has been made at the Paducah Gaseous Diffusion Plant[15] to provide sufficient data on the equilibria and rates of this reaction. Data obtained on the HF concentration–temperature equilibrium conditions are shown in Fig. V-1. These data extend the range of previous equilibrium measurements obtained by Briggs,[16] which are included in the figure for comparison. From these data, pro-

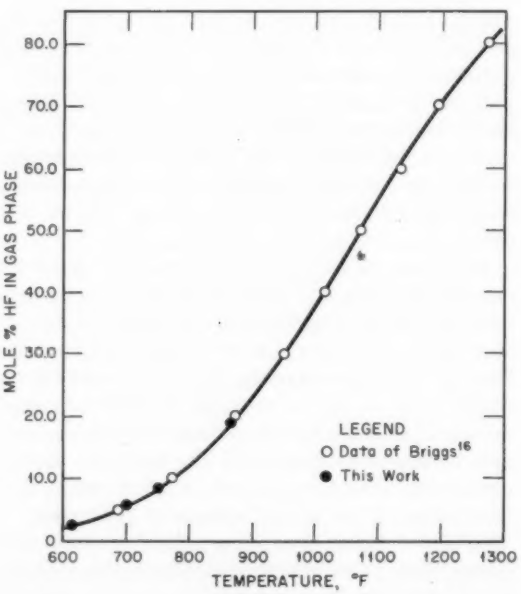

Fig. V-1 HF concentration–temperature equilibrium for the reaction $UO_{2(s)} + 4HF_{(g)} \rightleftharpoons UF_{4(s)} + 2H_2O_{(g)}$ *(Ref. 15).*

cessing conditions for operation with small HF excesses can be established; and calculations have shown[15] that lowering the HF concentration in the gas phase from 16.5 to 5 mole% will only decrease the percentage of conversion to UF_4 from 98 to 97.7.

Uranium Carbide

Methods for the Preparation of Uranium Carbide

Crane and Gordon[17] have summarized work performed by United Nuclear Corporation on the development of uranium carbide as a nuclear fuel. The alkane-gas–uranium-metal reaction was chosen for the synthesis of uranium carbide since the reaction produced a fine powder that could be pressed directly without prior comminution. The process also offered the advantage of low reaction temperatures (600 to 900°C), which is desirable from the standpoint of equipment design and construction. It was determined that the rate of heating, reaction temperature, and time at temperature must be carefully regulated to assure a specific carbon content in the product. The processing sequence that was established to give a UC product containing 4.7 wt.% carbon, <1500 ppm oxygen, and <300 ppm nitrogen is as follows: (1) hydride uranium metal at 200°C to produce a fine powder of UH_3; (2) introduce propane gas at 200°C and heat the retort vessel at the rate of 6.5°C/min to 400°C, 3.4°C/min to 550°C, and 2.1°C/min to 620°C; and (3) program the process so that the reaction time, including time at 620°C, is 130 min. The free carbon content in the product was maintained at <0.1 wt.% by employing copper components in the retort and by purging the system with argon gas immediately after completion of the carburization reaction.

The reduction of UO_2 with carbon *in vacuo* is an attractive alternative method for producing UC. Ainsley and associates[18] have observed that the reaction appears to be controlled by a diffusion process involving the migration of either oxygen or carbon through a UC layer. The rate of reaction was found to be insensitive to the particle size of UO_2 in the range 2 to 20 μ and to the particle size of carbon in the range 0.1 to 6 μ. Oxide particles >80 μ reacted at a significantly lower rate. The rate of reaction was sensitive to the presence of CO, and, therefore, it was necessary to remove the gaseous reaction products rapidly from the reactor.

A large-scale process for the production of uranium carbide suitable for arc melting into fuel slugs has been developed and demonstrated at Atomics International.[19] Uranium carbide having a carbon content of 4.6 ± 0.2 wt.% was produced by the high-temperature reduction of UO_2. Basically the process used for producing UC consisted of (1) blending ceramic-grade UO_2 and −200-mesh graphite powder to form a homogeneous mixture containing 11.55 wt.% carbon; (2) agglomerating the mixture with aqueous polyvinyl alcohol, the amount of alcohol added being 1 wt.% of the weight of UO_2 plus carbon; (3) drying the agglomerated mixture for 15 hr at 60°C in a vented oven; (4) heating the agglomerated mixture in a vacuum-induction furnace at 1950°C. Reaction and sintering of the UO_2-carbon mixture were carried out in a graphite crucible. The furnace was evacuated to 150 μ Hg pressure, heated rapidly to 1950°C, and maintained at 1950°C for 4.75 hr. The furnace was then cooled in an argon atmosphere for 15 hr or until the temperature of the UC product was <200°C.

During the high-temperature reaction, a coating of uranium carbide forms on the interior wall of the graphite crucible. This coating, upon reuse of the crucible, inhibits reaction between the charge and the crucible wall. The loss of uranium caused by this reaction is minimized by using a crucible repeatedly. It was proposed that the uranium lost by reaction with the crucible be reclaimed by treatment with water that converts the carbide coating to oxide.

Methods for synthesizing uranium monocarbide by the carbon reduction of U_3O_8 have been described by Lovell[20] and by Murbach and Strausberg.[21] The reaction was observed to proceed in two steps that involve formation of UO_2 as an intermediate compound. Details of the work of Lovell[20] have been reported in a previous issue of *Reactor Fuel Processing*.[22]

The results of a preliminary study have been reported by Oak Ridge National Laboratory (ORNL)[23] on the synthesis of uranium carbide by the gas-phase reaction of UF_6 with CH_4 and hydrogen using a plasma jet. Although UC was formed by a plasma jet at 2000°K and above, the yields were never greater than 1%. Attempts to increase the yields of UC were generally unsuccessful.

Sintering Properties of Uranium Carbide

Published work on the sintering of UC has indicated that densification of UC bodies to <90% of the theoretical density (13.6 g/cm^3) does not occur unless temperatures in excess of 1700°C are used. It is also indicated that high densities are often accompanied by the formation of carbon-deficient material. Chemical and mechanical sintering aids such as nickel[18,22] and plunge reaction sintering[24] were developed to avoid these effects.

Ainsley and associates[18] have investigated the effect of nickel addition on the sintering behavior of UC prepared from UO_2. The effect of 0.5 wt.% nickel on the densification of UC containing oxygen and free carbon is marked. In the absence of nickel, extensive gas evolution involving the loss of carbon and oxygen occurs during sintering. A pellet with a large fraction of open porosity is produced. With nickel present, gas evolution is slight, the levels of carbon and oxygen remain unchanged, and the final pellet has a high bulk density and a closed type residual porosity. The effect of nickel on the bulk density of sintered UC containing low concentrations of oxygen and free carbon appears to be slight. There are indications, however, that the presence of nickel increases the rate of sintering and enables the pellets to be heated to sintering temperature very rapidly. Although there is no explanation of the beneficial effect of nickel, the suppression of gas evolution suggests that nickel promotes the rapid sealing of pores during the early stages of sintering.

The factors affecting the sintering behavior of fine UC powders have been studied by McLaren, Regan, and Hedger.[25] Uranium monocarbide can be sintered consistently to densities 95 to 97% of theoretical at temperatures as low as 1550°C, provided that the carbide is milled to a high-surface-area powder before sintering. Handling and milling of the powder must be conducted in a high-purity inert atmosphere to minimize oxygen contamination. Powders contaminated with >0.2 wt.% oxygen generally sinter poorly.

Coating of Uranium Dicarbide

The encapsulation of individual nuclear fuel particles with ceramic coatings is being investigated, primarily for use in gas-cooled reactors. Both the fuel and fertile material for the Peach Bottom and Dragon reactors are in the form of ceramic-coated carbide particles uniformly dispersed in a portion of the graphite moderator. Reuter[26] has described the procedures used to apply a Duplex coating to UC_2 particles. This type of coating consists of two discontinuous layers of pyrolytic carbon. An inner coating is applied in a fluid-bed reactor by the pyrolysis of methane at 1400 to 1750°C. A very dense, more graphitic final coating is applied at 1800 to 2200°C.

Sowman and associates[27] have developed a method for coating UC_2 and $(U,Th)C_2$ particles in a rotating-drum system. The particles to be coated are prepared by the reaction of oxide granules (UO_2 or UO_2-ThO_2) with excess carbon or graphite powder at 2500 to 2600°C. Since the temperature of reaction is above the melting point of the carbide, spheroidization takes place by virtue of the surface tension of the molten drop. The carbide particles were coated in a rotating graphite drum heated by induction. A hollow shaft of the drum provided the means of gas entrance. In addition to gas flow rates and temperature, important variables affecting coating quality were rate of drum rotation, drum diameter, and quantity of particles loaded in the drum. With the proper balance of these factors, uniformly coated spherical particles were produced (see Fig. V-2).

Application of fluidized beds to the coating of carbide fuel particles is being studied at

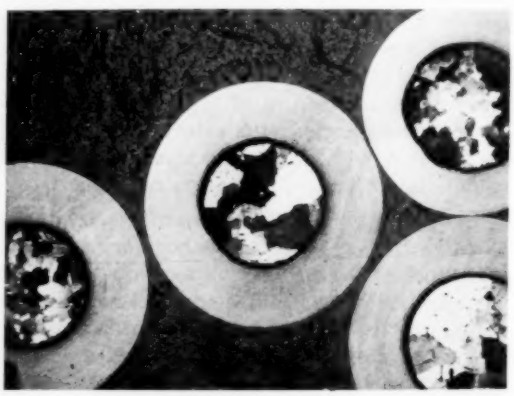

Fig. V-2 Batch of particles coated in a rotating drum with pyrolytic carbon (not highly oriented). The particles are ~175-μ UC_2 and ~80-μ pyrocarbon.[27] (Reprinted by permission from Nuclear Science and Engineering.*)*

ORNL.[28] A cutaway view of the furnace and fluid-bed apparatus used in coating studies up to 2000°C is shown in Fig. V-3. The furnace is heated by a graphite resistor. The temperature of the furnace is controlled by an optical pyrometer that sights the graphite reactor. The coating procedure consisted of (1) heating the furnace to the coating temperature while purging with helium, (2) adjusting the carrier-gas flow to a rate sufficient to fluidize the particles, (3) adding the charge of particles, (4) readjusting the gas flow to supply the proper ratio of hydrocarbon to carrier gas, and (5) operating until the proper coating thickness is applied.

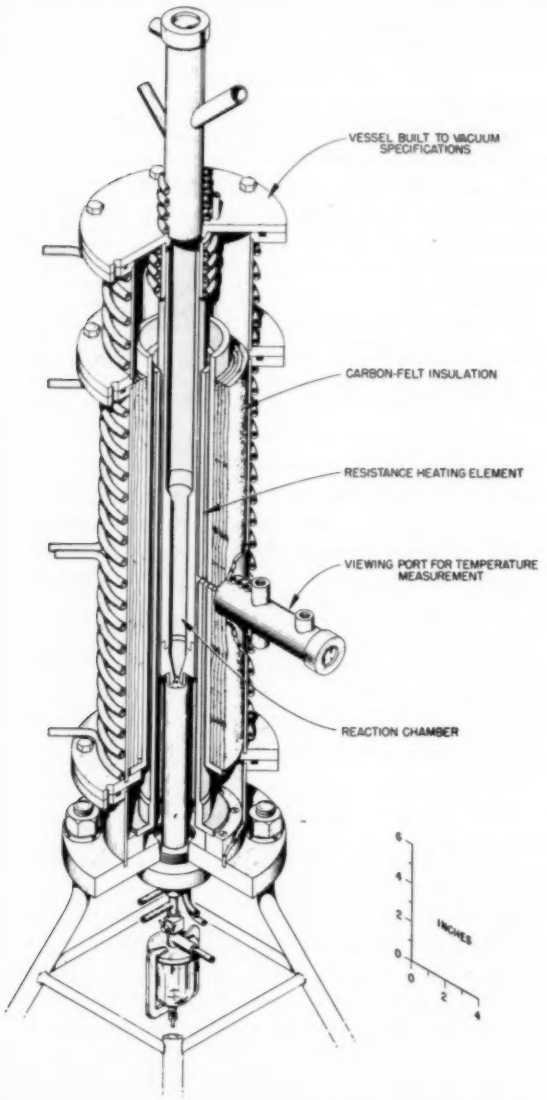

Fig. V-3 High-temperature fluidized-bed particle-coating apparatus.[28] (Reprinted by permission from Nuclear Science and Engineering.*)*

The nature of the carbon coating was affected by the rate of coating. At coating rates less than 18 μ/hr, a predominantly columnar structure was obtained; at higher rates, the structure was laminar. Pilloton[29] has prepared calculations of gas-flow requirements and of other parameters for the fluidized-bed particle-coating process.

Pyrolytic carbon coatings provide excellent protection for uranium carbides against attack by moisture. A series of tests performed at ORNL[30] on UC_2 particles coated with laminar type pyrolytic carbon showed that this coating protects against prolonged exposure to water vapor below 800°C. Rapid failure of the coatings occurred at 1100°C. Blocher et al.[31] at Battelle Memorial Institute have recently reviewed the technology of preparing ceramic-coated nuclear fuel particles and the performance of these particles in radiation and high-temperature environments.

Uranium Nitrides, Phosphides, and Sulfides

Preparation and Properties of Uranium Mononitride

Uranium mononitride has many favorable characteristics that make it potentially attractive as a nuclear fuel. In powder form it is not nearly as reactive with the atmosphere as UC. The compatibility of UN with cladding materials is superior to that of uranium monocarbide.[32] The development of uranium and plutonium nitrides as possible fuels for fast-breeder reactors is subject to the technical feasibility of producing these compounds on a large scale. Anselin[33] has reviewed methods for preparing UN and PuN and has discussed the physical properties of these materials. Uranium mononitride can be prepared by direct combination of the elements. Hydrided uranium metal is heated in pure nitrogen under pressure at 400°C to form $UN_{1.77}$. Uranium mononitride is obtained by dissociation of $UN_{1.77}$ under vacuum at temperatures >800°C.

Preparation of UN in Fluid-Bed Reactor

Uranium nitride has been prepared at Harwell using fluid-bed techniques.[34] The preparation involved the carbothermic reduction of UO_2 in a stream of nitrogen at 1500°C. The reaction proceeds according to the equation:

$$UO_2 + 2C + \tfrac{1}{2}N_2 \rightarrow UN + 2CO$$

Two distinct processes were studied: (1) the hydrocarbon route, in which the carbon was fed continuously into a fluid bed of UO_2 in the form of a hydrocarbon vapor dispersed in the fluidizing gas; and (2) the carbon route, in which the reaction vessel was loaded initially with a charge composed of an intimate mixture of powdered UO_2 and carbon in the required proportions.

In tests investigating the hydrocarbon route, benzene was the source of carbon. Optimum reaction occurred at 1450 to 1500°C. At higher temperatures the fluid bed sintered, and at lower temperatures (<1200°C) the particles became coated with an impervious layer of pyrolytic carbon. Complete conversion of UO_2 to carbonitride (UC_xN_{1-x}) was not possible at high benzene feed rates because coating occurred after only partial conversion, even at 1500°C. At lower feed rates the reaction proceeded normally until the fraction of UO_2 converted was 60%. At this point the bed began to adhere to the wall of the reactor. Methods employed for preventing this adherence were generally unsuccessful. The product from runs of high conversion, apart from residual UO_2, consisted mainly of a single-phase carbonitride, UC_xN_{1-x}, where x was as high as 0.3 to 0.4. The rate of carburization during most of the reaction period was much slower than that of nitridation. During the initial reaction period, the product had a nitrogen-to-uranium mole ratio of 0.85, and the carbon-to-uranium mole ratio was 0.1. Further reaction resulted in carburization at the expense of nitrogen in the carbonitride, as well as carburization of the residual oxide.

In investigations of the carbon route, UO_2 and carbon black were blended, fabricated into pellets, and fluidized in a stream of nitrogen at 1450 to 1500°C. Products having nitrogen-to-uranium mole ratios of 0.96 were prepared from starting materials having a carbon-to-UO_2 mole ratio between 1.65 and 1.75. The apparent carbon deficiency was made up by attrition of the surface of the graphite reactor. When the carbon-to-UO_2 mole ratio in the starting material was increased above 1.75, the nitrogen-to-uranium mole ratio of the product decreased with a concomitant increase in the carbon-to-uranium mole ratio. In the preparation of uranium carbonitrides that were rich in carbide, yet free from uncombined carbon, it was necessary to control not only the carbon-to-UO_2 mole ratio in the starting material but also the partial pressure of nitrogen in the fluidizing gas. Details of preparations of carbonitrides covering a wide range of composition appear in Table V-1.

Table V-1 COMPOSITION OF URANIUM CARBONITRIDES PREPARED IN A FLUID-BED REACTOR[34] AT 1450°C

Reagents			Product	
Run No.	C/UO_2 mole ratio	Fluidizing gas	Formula	X-ray parameter,* A
35	1.63	N_2	$U(C_{0.07}N_{0.94})$	4.895
36	2.17	N_2	$U(C_{0.33}N_{0.69})$†	4.917
45	2.80	Ar/N_2 (1000/1)	$U(C_{0.90}N_{0.97})$	4.961
42	2.80	Ar/N_2 (10,000/1)	$U(C_{0.97}N_{0.93})$	4.960

*Rock-salt structure.
†Contained 0.12 wt.% uncombined carbon.

For the preparation of uranium carbonitrides, the carbon route has the advantage that carbonitrides, UC_xN_{1-x}, have been prepared in which x has values between 0.04 and 1.00. The hydrocarbon process yielded carbonitrides in which x varied unsystematically between 0.2 and 0.3. The carbon process appears preferable as a manufacturing route since (1) the carbon content of the reactants can be rigorously controlled, (2) sintering problems are relatively absent, and (3) a shorter reaction time is required.

Properties of UN

Workers at the Albany Metallurgy Research Center[35,36] of the U. S. Bureau of Mines are investigating the UC-UN-UO ternary system to obtain data for the evaluation of potential high-temperature reactor fuels. In other work Sano et al.[37,38] have determined the conditions for the formation of stable solid solutions of UC and UN. It was observed that the composition of the system was determined by the nitrogen pressure and temperature.

The preparation of UN by the reaction between uranium metal and nitrogen is usually accomplished by the decomposition of an in-

termediate compound, U_2N_3. Lapat and Holden[39,40] have measured the equilibrium decomposition pressures of U_2N_3 from 600 to 1100°C and nitrogen-to-uranium mole ratios from 1.7 to the two-phase region UN + U_2N_3. The heat of decomposition of U_2N_3 to UN and nitrogen gas was determined to be 57 kcal per mole of N_2. Thermodynamic functions for the formation of U_2N_3 from UN and nitrogen have been calculated by Bugl and Bauer[41] on the basis of vapor-pressure measurements over UN-U_2N_3 mixtures. In a recent paper, Bugl and Bauer[42] published the results of a study of the phase relations in the uranium-nitrogen system.

The oxidation kinetics of UN in CO_2, oxygen, and water-saturated air were determined by Bugl and Bauer[43] to be linear, with activation energies between 10.4 and 15.4 kcal per mole of UN. The oxidation product at temperatures above 300°C is U_3O_8. At 300°C, UN corrodes in water to form UO_2. The rate of corrosion is highly sensitive to composition and density of the UN. At 100°C, corrosion rates in water are negligible. Moreau and Philippot[44] have observed that the reaction between oxygen and UN at 350 to 480°C yields an oxide with a composition between U_3O_8 and UO_3. They found that the reaction obeys linear kinetics, with an activation energy of 24.5 kcal per mole of UN.

Uranium Phosphides

The desire for greater efficiency in reactor operation has prompted investigators at Argonne National Laboratory (ANL)[45] to make a search for nuclear fuels that can withstand high burnups at increasingly higher operating temperatures. Uranium monophosphide appears attractive as a fuel because of its high degree of thermal stability and high melting point.

In initial studies at ANL,[45] UP was prepared by the vacuum reaction of finely divided uranium metal with red, amorphous phosphorus. The reaction was highly exothermic and resulted in a phosphorus-deficient UP clinker. The main disadvantage of this method is the difficulty of obtaining a high-purity product. Oxygen contents of 1.1 wt.%, corresponding to 9% UO_2, were the lowest values obtained in these studies.

A preparative method based on the reaction of phosphine gas (PH_3) with finely divided uranium, which was derived from uranium hydride, was more successful in producing a high-purity material.[45,46] The highest yields resulted when the reaction was carried out at 385°C using a plutonium-to-uranium mole ratio slightly greater than unity. X-ray diffraction analyses of the black product revealed the presence of only U_3P_4. This material, when heated at 1400°C under vacuum to drive off excess phosphorus, produced homogeneous, single-phase UP products containing 0.16 to 0.35 wt.% oxygen. Sintered bodies of UP with 92 to 93% of the theoretical density were achieved by heating pressed pellets at 2000°C for 1 hr.

Uranium monophosphide is the most stable of the three compounds in the uranium-phosphorus system.[46] The diphosphide, UP_2, decomposes rapidly above 700°C; U_3P_4 decomposes in vacuum to UP and phosphorus at 1100°C. Uranium monophosphide melts at 2540°C in hydrogen and has a sufficiently low vapor pressure at this temperature that it can be arc melted readily. The monophosphide has a NaCl type crystal structure and a lattice constant of 5.589 A, corresponding to a theoretical density of 10.23 g/cm^3.

Uranium Sulfides

A material that appears attractive as a high-temperature fuel is uranium monosulfide that has a uranium density comparable to that of UO_2 and a cubic structure that is stable to its melting point of 2460°C. Shalek and Handwerk[47] at ANL have prepared high-purity US by a two-step method. In the first step the uranium metal is hydrided, the hydride is decomposed to give a fine powder, and the powdered metal is treated at 400°C with a measured volume of H_2S to give a product containing a mixture of uranium metal and uranium disulfide (US_2). In the second step the mixture is blended and heated to 1800°C in a vacuum or in an argon atmosphere to produce US. To produce high-purity US in high yield, the workers found it necessary to use (1) several hydriding-dehydriding reactions to produce a powder of very high surface area and (2) a temperature of not more than 400°C for both the hydride decomposition and the H_2S reaction to prevent coalescence of the reacting powder. When these precautions were observed, a product containing 99.8 wt.% of the US phase was obtained.

Sinterability of US is markedly affected by the presence of secondary phases.[46,47] The

presence of small amounts of UOS aids densification through the mechanism of liquid-phase sintering and results in products with densities as high as 95% of theoretical. High-purity US sinters to only 85% of the theoretical density. Oxygen contamination in pure US appears as discrete UO_2 particles in the US phase upon sintering.

Production of Thorium Compounds

Thorium Oxide

In a report on the preparation of ceramic-grade thorium-uranium oxide for use as reactor fuel material, Cogliati et al.[48] have described a process based on (1) the reduction of U(VI) to U(IV) in aqueous nitrate solutions containing uranium and thorium, followed by (2) precipitation of the mixed oxalates. In the first step of the process, $UO_2(NO_3)_2$ is reduced to U(IV) nitrate by hydrogen produced by dissociation of formic acid on a platinum black-on-alumina catalyst. If a high rate of dissociation of formic acid and, in turn, a high rate of reduction of U(VI) to U(IV) are maintained, a temperature of 50 to 60°C is employed. At this temperature, U(IV) nitrate is unstable and urea (10 g/liter) is added to stabilize the uranium in the (IV) valence state. Thorium and uranium are recovered from the nitrate solution in the second step by precipitation with oxalic acid. A specific excess (10%) of oxalic acid is used to produce a precipitate that settles and filters rapidly. Uranium losses to the filtrate in pilot-plant tests were generally less than 1 mg/liter.

The mixed oxalates are fired to oxides between 500 and 900°C. The firing temperature and the nature of the atmosphere (reducing or oxidizing) appear to have little effect on the sintering properties of the oxide product, although it was observed that firing in a hydrogen atmosphere promotes solid-solution formation.

Sol-Gel Process

Dense particles of ThO_2, which are suitable for vibratory compaction into tubes and have a bulk density approaching 90% of theoretical, have been prepared at ORNL by a sol-gel process.[49,50] The starting material for the sol-gel process is a $Th(NO_3)_4$ solution. There are four steps to the process (see Fig. V-4): (1) drying and denitration of the nitrate to oxide; (2) dispersion of the oxide to a hydrosol; (3) conversion of the sol to a gel by evaporation of the water; and (4) densification of the gel by calcination. The shape and size of the particles are established in the gel and are retained in subsequent steps except for shrinkage during calcination. For the preparation of mixed uranium-thorium oxide, $UO_2(NO_3)_2$ solution is added at the sol-formation step. In the prepara-

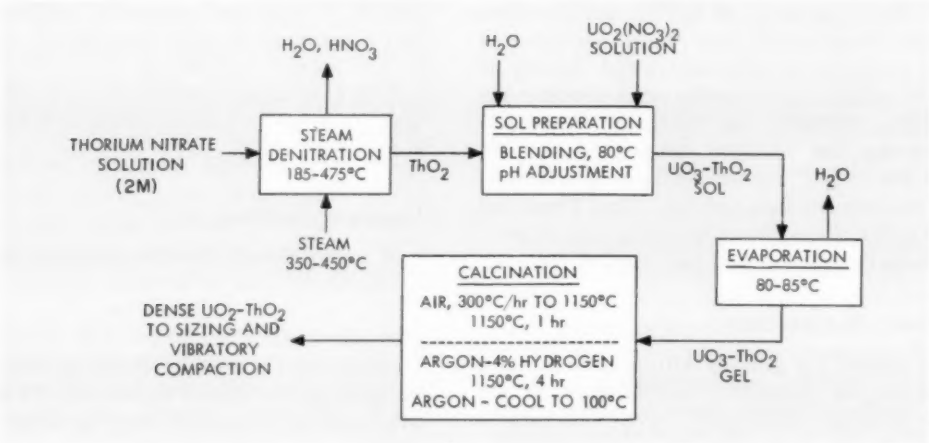

Fig. V-4 Schematic flow sheet for the sol-gel process.[49]

tion of mixed oxide with a uranium content of 10% or less, uranium may be added as the nitrate to the $Th(NO_3)_4$ solution.

The oxide for sol preparation is made from $Th(NO_3)_4$ by drying and denitration in a steam atmosphere. The critical factors for the production of an oxide that is readily dispersed in water are temperature, which must be carefully regulated to prevent local overheating, and agitation, which must be sufficient to permit contact of the oxide with steam. The drying-denitration step has been demonstrated at ORNL on an engineering scale in a rotary calciner. The calciner is a stainless-steel drum 14 in. in diameter and 31 in. long which rotates inside a cylindrical 14-kw electric heater. Sufficient $Th(NO_3)_4$ is introduced to the calciner to produce 15 to 20 kg of ThO_2, and the drum is heated to 200°C in an air atmosphere. When this temperature is reached, the air is replaced by superheated steam and the temperature is raised to 475°C. Steam denitration is continued at 475°C for 3 hr. The product is a free-flowing powder with a residual nitrate concentration of 0.03 mole per mole of ThO_2.

The ThO_2 product is dispersed in dilute HNO_3 by agitation and digestion at 80°C for 1 hr. The conditions for forming a good sol of pure ThO_2 are not rigorous; *p*H values between 2.0 and 4.5 are satisfactory. Stable free-flowing sols have been prepared containing up to 7*M* ThO_2. When uranium is present, the *p*H of the system must be carefully controlled to assure uniform distribution of uranium in the thoria.

The thoria sol is converted to a glassy gel by careful evaporation, the primary requirement being evaporation without boiling. This has been successfully accomplished by surface evaporation in shallow trays. On reaching the solid state, the material breaks into fragments, the size of which varies with the depth of material in the drying tray. With 0.75 in. of 2*M* ThO_2 sol in the drying tray, the product gel is predominantly −6 +20 mesh. Fine particle-size material is obtained by grinding the gel in a ball mill.

Thorium oxide particles having >99% of the theoretical density are obtained by calcination of the thoria gel in air for 1 hr at 1150°C. The recommended calcination procedure is to raise the temperature of the gel to 1150°C at a rate not exceeding 300°C/hr. With the mixed uranium-thorium oxide, calcination in air gives a uranium oxide with a composition between UO_2 and U_3O_8. Therefore an additional 4-hr calcination period in an argon atmosphere containing 4% hydrogen is required to reduce the uranium oxides to UO_2.

A recent development at ORNL is the adaptation of the sol-gel process to the preparation of microspheres of the oxides (or carbides) of thorium or mixed thorium-uranium.[49–51] The formation of microspheres is accomplished by dispersing the sol into an immiscible organic solvent, such as carbon tetrachloride or 2-ethyl-1-hexanol. The solvent partially dehydrates the sol droplets by extracting water, and rigid gel microspheres are produced.

The engineering feasibility of producing spherical thoria particles with diameters of 100 to 1000 μ was demonstrated[51] in a fluidizing column (see Fig. V-5) in which 2-ethyl-1-hexanol was the dispersing and drying agent. The sol is introduced at the top of the column

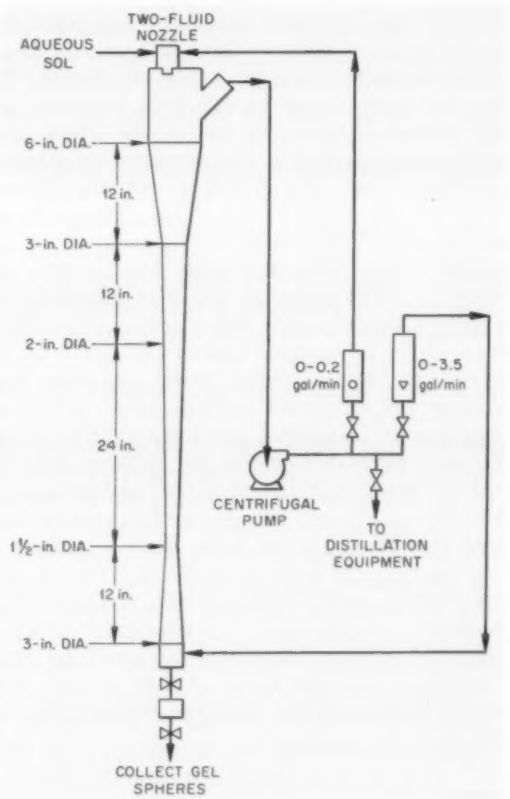

Fig. V-5 Schematic flow diagram of equipment for producing gel spheres from aqueous sol.[51]

through a two-fluid spray nozzle and is dispersed into droplets. The droplets are allowed to settle in the tapered column until they reach fluidization velocity. Coalescence of the droplets and wetting of the glass column are prevented by adding a suitable surface-active agent to the organic solvent. As water is extracted from the sol droplets by the organic phase, a partial gelling or setting of the droplets occurs with a concomitant increase in density. The dense gel spheroids are collected at the bottom of the column after a holdup of 10 to 30 min. The gelled particles are dried at 100°C to remove solvent and to reduce the water content to 5 wt.%. After being fired at 1150°C, the thoria and thoria-urania spheroids produced in the fluid-bed facility have near theoretical density and very high crushing strengths.

Thorium Carbide

The fuel and fertile material for the Peach Bottom High-Temperature Gas-Cooled Reactor (HTGR) are carbides uniformly dispersed as particles in a portion of the moderator. A process has been developed at General Atomic[52-54] for the preparation of $(Th,U)C_2$ particles by the carbon reduction of the oxides. First, agglomerated particles are prepared by mixing powdered ThO_2, UO_2, graphite, and ethyl cellulose in trichloroethylene to form a slurry. Next the particles are dried at 60°C and sieved to obtain a size fraction between 300 and 420 μ in diameter. The particles are then dispersed in graphite flour, loaded into a graphite crucible, and heated in vacuum between 2100 and 2300°C (see Fig. V-6). Under these conditions the oxides are converted to dicarbides. After the reaction is complete, the temperature of the furnace is raised above the melting point of the carbides (2450°C) to densify and spheroidize the particles. The powdered-graphite bed prevents the particles from flowing or sintering together and actually produces a thin graphite coating on the surface of the particles. The particles are separated from the graphite powder by sieving. Particles prepared by this method were found to be of high density, and the results of X-ray analyses showed them to be $(Th,U)C_2$.

Preparation of ThC_2 Spheres by Sol-Gel Process

A recent application of the sol-gel process has been the preparation of spherical ThC_2 and $(Th,U)C_2$ particles.[49-51] Carbon black with a particle size of 90 to 290 A is blended at high shear with a $2M$ ThO_2 sol at 20°C. Mild agitation of the sol for 30 min at 55°C is required to produce a stable, homogeneous suspension. The preparation of dicarbides requires that 4.4 moles of free carbon per mole of metal be added to the sol. Sols prepared by this procedure were used to make microspheres of $(Th,U)C_2$ having diameters of 30 to 1000 μ and containing 0 to 20 at.% uranium. The formation of carbide microspheres is accomplished by dispersing the sol in an organic solvent (2-ethyl-1-hexanol) as in Fig. V-5. A secondary alcohol (2-octanol) is added to the solvent to suppress the tendency of the solvent to extract carbon along with the water. The gel is dried in vacuum for 2 hr at 40°C to remove excess solvent and water. The oxide-carbon gel is converted to dicarbide microspheres by heating at 1750°C for 6 hr in a vacuum or in an argon atmosphere. Kinetic studies[51] have shown that the carburization reaction is first order, with an activation energy of 112 kcal per mole of ThO_2.

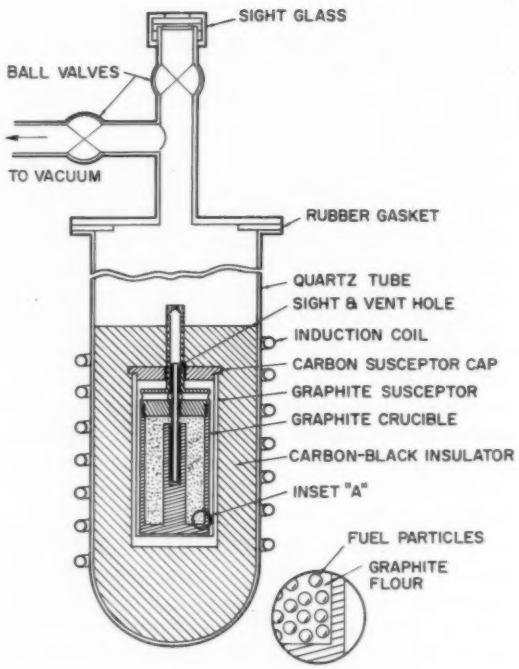

Fig. V-6 Schematic diagram of conversion furnace for production of $(Th,U)C_2$ spheres.[53]

Carbon Coating of Thorium Carbide Particles

Thorium-uranium dicarbide is extremely reactive to moisture. Fuel compacts containing unprotected $(Th,U)C_2$ disintegrate by hydrolysis after a few hours' exposure to air. A process for coating $(Th,U)C_2$ particles with carbon films to protect the carbide against attack by water vapor has been developed at General Atomic.[52,53] Coating is accomplished in a fluidized-bed apparatus,[52] using a methane-helium mixture (0.1 to 0.25 atm CH_4) at 1400°C. A method for coating $(Th,U)C_2$ particles based on the application of three layers of pyrolytic carbon (Triplex coating) has been described by Chin et al.[53] Triplex pyrolytic carbon coatings consisted of an inner spongy layer, a middle layer of laminar pyrolytic carbon, and an outer layer of columnar pyrolytic carbon. The inner layer was applied to pyrolysis of acetylene (80 vol.% in helium) at 1100°C; the laminar coating was deposited by pyrolysis of methane (18 vol.% in helium) at 1700°C; and the columnar outer layer was applied by pyrolysis of methane (2.5 vol.% in helium) at 1800°C.

In general, the procedures that have been developed for carbon coating of uranium carbide particles[26-28] are applicable to the coating of ThC_2 or $(Th,U)C_2$. Bomar and Gray[55] at ORNL have described the pertinent results of research and development on thorium-uranium carbides for coated-particle reactor fuels. Carbon coatings were applied[55] to $(Th,U)C_2$ particles by pyrolysis of methane in the fluid-bed reactor (see Fig. V-3) that was also used in UC_2 coating studies.[28]

Phase Diagrams in Th-C Systems

Since thorium carbide systems are becoming of increasing technical importance for the development of nuclear reactors, knowledge of their physical properties is of practical interest. The results of an extended investigation of the thorium-carbon system in the region from the monocarbide to 80 mole % carbon have been reported by Langer et al.[56] Thorium dicarbide exists from 8 to 9.56 wt.% carbon ($Th_{2.04}$), in contrast to the normally substoichiometric UC_2. X-ray and metallographic evidence indicates that a two-phase region exists between the monocarbide and dicarbide. This region extends from 6.5 to 8 wt.% carbon.

Bomar and Gray[55] and Hill and Cavin[57] have investigated the phase relations in the UC_2-ThC_2 system. The results of this study have shown that ThC_2 will dissolve up to 25 wt.% UC_2 without change in lattice structure. Similarly, UC_2 dissolves up to 30 wt.% ThC_2 while retaining the body-centered tetragonal structure. Between these two solid solutions there is an area of single phase with a structure that can be indexed as orthorhombic or face-centered tetragonal.

Thorium Sulfide and Other Ceramic Materials

Preparative methods and properties of several thorium and thorium-uranium compounds have been studied by Farkas et al.[58,59] to provide a preliminary evaluation of these materials for use as thermal-breeder fuels. The compounds Th_2Al, ThB_4, $ThBe_{13}$, ThC, ThC_2, Th_3Si_2, and ThSi, with and without additions of their uranium counterparts, were prepared by arc casting. With the exception of the aluminide, the uranium substituted for the thorium by solid-solution formation. The borides and beryllides were the most resistant to oxidation in dry air and CO_2 up to 540°C. However, above 540°C, the beryllides oxidized rapidly in dry air.

Thorium monosulfide is being investigated at ANL to ascertain its potential as a nuclear fuel.[45] The monosulfide is prepared by the reaction of H_2S gas at 700°C with finely divided thorium-metal powder.[47,60] A highly reactive metal-powder feed is prepared by hydriding metal turnings at 200 to 500°C and then dehydriding at 750°C. The product of the reaction with H_2S consists essentially of equal parts of ThS_2 and thorium metal. This material is blended and heated to 1800 to 1900°C in vacuum to produce ThS. Because of the great affinity of ThS for oxygen at elevated temperatures, it was not possible to produce ThS in high purity.

A method for the preparation of ThS_2 by the reaction of ThO_2 with H_2S in the presence of carbon has been reported by Sansonov and Dubrovskaya.[61] At temperatures below 1200°C, the product contains a ThOS phase, and only by prolonged reaction at 1300°C is ThS_2 produced. In the absence of carbon, the reaction of ThO_2 with H_2S proceeds to the formation of $ThS_{1.7}$. The disulfide does not appear to be formed.

Work at ANL[45] is continuing on the preparation and characterization of thorium phosphide as a nuclear fuel. The material is prepared by

reaction of hydrided thorium metal with phosphine at 550°C to produce Th_3P_4, which is decomposed at 1300°C to give a homogeneous ThP product. (J. Barghusen)

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Section

VI

Reactor Fuel Processing

Safety in Chemical Processing

In the previous issue of *Reactor Fuel Processing*,[1] details were reported of an incident involving a fire and the venting of an overpressured plutonium anion-exchange contactor in the plutonium-purification facility for the Redox plant at Hanford. The significance of this event was the realization that the maximum safe operating temperature for plutonium anion-exchange systems is substantially lower than previously thought and that nitrate-loaded resin flooded with liquid is capable of violent decomposition. Also reported in the same Review was a description of an accident that occurred in France in 1962 involving the rupture of a plutonium anion-exchange contactor. A final report on this accident has been made available in a U. S. Atomic Energy Commission (USAEC) translation.[2]

Incident Involving a Plutonium Anion-Exchange Contactor at Rocky Flats

On July 14, 1963, a noncriticality incident occurred at the USAEC Rocky Flats plant which involved pressurization of a batch anion-exchange contactor and subsequent rupture of a gasket and discharge of the column contents. Fire followed the release of the contents into the air atmosphere of the glove-box enclosure. Although this incident was similar in many respects to that which occurred at Hanford, details of the incident are reported here to point out certain hazards associated with the use of anion-exchange resins in plutonium service. The descriptions reported here are based on the findings of a committee formed specifically to investigate and review the event.[3,4]

Description of Process Equipment

At Rocky Flats all plutonium-bearing residues from processing operations are recycled for plutonium recovery by hydrometallurgical techniques. In the recovery process, separation of plutonium from americium (decay product of ^{241}Pu) is achieved by precipitation of plutonium as the peroxide from a $2N$ nitric acid solution. The filtrate, which contains the americium and a small quantity of plutonium, is processed for plutonium recovery by ion-exchange techniques. The solution is concentrated to $7N$ to $8N$ HNO_3 and 40 g of plutonium per liter by evaporation and then is fed to a system of three anion-exchange contactors operated in series. Each contactor is constructed of 7-in.-OD pyrex glass pipe, 30 in. long, with stainless-steel top and bottom fittings. Teflon gaskets are used to make the seals between the glass pipe and metal flanges. The flange at the bottom of each column is fitted with an O-ring groove. The groove contains a Tygon O-ring that bears against the Teflon gasket to provide the seal. The columns are loaded with 50- to 80-mesh Dowex 1-X4 anion-exchange resin that is supported by a stainless-steel plate containing 100-mesh screen inserts. The glass columns are provided with external shielding of $\frac{1}{8}$-in.-thick lead.

Operation of the anion-exchange facility is carried out on a batch basis in four steps: (1) plutonium is absorbed on the resin as the $Pu(NO_3)_6^{2-}$ complex while the americium passes through the system unaffected, (2) impurities are removed from the plutonium-loaded resin by a $7N$ HNO_3 scrub stream, (3) purified plutonium is eluted from the resin by a $0.35N$ HNO_3 wash solution, and (4) the resin is converted to the nitrate form by washing with $7N$ HNO_3. Although the operating procedure specified heating all solutions entering the anion-exchange

facility to 57 ± 2°C, this procedure had not been followed precisely for several years. The operation was carried out at ambient temperature (25 to 30°C). The plutonium product from the anion-exchange recovery operation is recycled to the peroxide precipitation step. Plutonium concentration in all process streams in the anion-exchange facility is continuously monitored by colorimeters.

All operations involving handling of plutonium are carried out in fully enclosed glove boxes designed for the containment of alpha contamination. The glove boxes are fabricated of 16-gauge stainless steel, and all windows are constructed of ¼-in.-thick Plexiglas 5009. In certain cases, an additional layer of ¼-in.-thick lead glass has been installed on the windows to reduce gamma-radiation exposure. All process equipment in the area in which the incident occurred is designed to be nuclearly safe for any concentration of plutonium solution.

Description of the Incident

During the first working shift on July 14, 1963, the resin in three anion-exchange columns (column numbers 356, 357, and 358) was converted to the nitrate form using standard procedures. After the resin was conditioned, solution was fed to the column. After column 356 was fully loaded with plutonium solution containing 8*N* HNO_3 and 40 g of plutonium per liter, the feed was shut off while a plutonium colorimeter was calibrated. All valves on columns 357 and 358 were closed. The vent valve and the inlet and outlet valves on column 356 were closed. The valve in the feed line from the feed tank to column 356 was also closed.

Approximately 4 hr after the feed was shut off, workers in the area heard a muffled report from the filtrate recovery facility. The glove box was immediately filled with brown fumes characteristic of oxides of nitrogen. A second muffled report occurred 30 sec later, and at this time a fire was observed adjacent to column 356. The flames extended to the top of the enclosure and ignited gloves on the front and at the top of the glove box. The fire was extinguished within 90 min by CO_2 and magnesium oxide sand. The latter was a most effective agent in extinguishing burning gloves.

No major equipment damage resulted from the fire. Destruction was mainly associated with the Plexiglas 5009 windows and gloves at the front and at the top of the box; these items were replaced. Also destroyed in the fire were several liquid transfer lines (thin-walled plastic hoses) connected to column 356. There was no damage or visible effect of heat on the liquid feed pump, the pyrex-glass columns, the lead shields, or any of the Teflon gaskets on the ion-exchange columns. The Tygon gasket on the bottom flange of column 356 was ruptured, and observations of the gasket after the fire showed that the gasket experienced significantly greater damage on the inner surface than on the outer surface.

The major consequence of the fire was contamination of the immediate area with plutonium- and americium-bearing dust. No significant reduction in the output of the plutonium-metal production plant resulted from the accident, and the filtrate recovery anion-exchange facility resumed operation after five days. No injuries, radiation or otherwise, resulted from the incident.

Analysis of Evidence and Findings

Immediate observation of the three ion-exchange columns indicated that column 358 was unaffected by the fire and that column 357 had red-brown fumes containing NOCl and NO_2 in the air space above the resin bed. At the time of the accident, column 356 contained 6 liters of Dowex 1-X4 resin loaded with 400 g of plutonium and 4 liters of 8*N* HNO_3 solution containing 40 g of plutonium per liter. After the fire the column contained only 2 in. of resin and no liquid. Most of the resin remaining in the column was blackened, and microscopic examination showed that the resin beads were fused rather than fractured. Subsequent laboratory tests indicated that a temperature of at least 500°C was required to convert a green plutonium-loaded bead to the black fused form.

The following explanation has been offered[3,4] to describe the incident:

Although the exact primary source of ignition has not been determined, it appears likely that the reaction started inside anion-exchange column 356. The reaction probably involved the oxidation by nitric acid of loaded Dowex 1-X4 resin or some extraneous organic material introduced into the column with the feed stream, such as hose plasticizer. (It is known that hot nitric acid solutions will leach plasticizer and plasticizer decomposition products

from thermoplastics. Plasticizers are esters that can produce alcohols upon reaction with acid.) The reaction between nitric acid and resin or plasticizer resulted in pressurization of the exchange column and in the subsequent rupture of the Tygon gasket. Anion-exchange resin and solution were discharged from the column through the ruptured gasket. Hot, partially oxidized material expelled from the column ignited in the air atmosphere of the box and produced the flash fire. This fire then ignited gloves and hoses in the immediate area.

As a result of its study of the accident, the investigating committee recommended[4] that equipment, such as anion-exchange columns where gas evolution is known to occur, should be equipped with rupture disks or other pressure-relief devices. Operating procedures on anion-exchange columns should include provision for venting the system during temporary as well as prolonged shutdowns. The committee also emphasized the effectiveness of magnesium oxide sand in extinguishing burning embers from gloves during the fire. The committee recommended that the magnitude and causes of gas evolution from plutonium-loaded anion-exchange resins be determined in laboratory tests. It was also suggested that the compatibility of nitric acid with plutonium-loaded resin be the subject of a laboratory investigation.

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